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THE ELASTIC EXTENSIBILITY OF MUSCLE[1]

BY GEORGE W. F. BRISBIN[2] AND FRANK ALLEN[3]

Abstract

Measurements of the extensibility of muscles and other tissues were first made, as far as the authors are aware, by Wertheim in 1846. He proposed for them a hyperbolic law of elasticity of the form: $y^2 = ax^2 + bx$. Further measurements were made at much later dates by Marey and by Howell, who did not attach to them any mathematical law of elasticity.

The present writers have investigated the elasticity of muscles again, and have found that their own data, as well as those of previous investigators, conform to the logarithmic law,

$$E = k \log W + c,$$

where E is the extension, W the stretching force, and k and c are constants.

This law is found to hold for muscles both striped and plain, and for nerve tissue. It seems to be true for all tissues except bone which, according to Wertheim, follows Hooke's law of elasticity for inorganic elastic matter.

One of the earliest, if not the first, quantitative investigations of the extensibility of the principal tissues chiefly of the human body was made in 1846 by Wertheim (15). His researches were very extensive and comprised numerous experiments on the comparative elasticities of bone, nerve, tendon, vein, and muscle from both human and canine sources, some of which were obtained immediately after death and others about five hours later. From his paper nothing can be gathered concerning the methods which he used to apply the stress to the tissues. Since, after death, chemical changes of a complex nature occur in all tissues, subsequent investigators have preferred to work with materials taken from the living animal.

Wertheim found that his measurements, when plotted with the stretching weights as abscissae and the corresponding extensions as ordinates, formed not a straight but a curved line which appeared to be approximately a hyperbola of the form given by the equation:

$$y^2 = ax^2 + bx,$$

where y represents extensions of the tissue in millimetres, x the stress in kilograms per square millimetre of its cross section, and a and b are constants. Since of necessity there is no extension when there is no stress, or $y = 0$ when $x = 0$, the vertex of the curve occurs at the origin of co-ordinates. From

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the graph Wertheim obtained numerical values of the constants, which have an extraordinary range in magnitude for different tissues as the following equations show:

$$\text{Muscle, } y^2 = 14{,}549{,}333\,x^2 + 23{,}863\,x$$
$$\text{Vein, } y^2 = 1{,}174{,}780\,x^2 + 193{,}970\,x$$
$$\text{Artery, } y^2 = 257{,}747{,}000\,x^2 + 5{,}784{,}200\,x.$$

With constants of such great magnitude, the equation could be forced to agree with the curve. As the constants are concerned chiefly with changes in the physiological properties that occur in tissues when being stretched, they have probably small numerical values. It is difficult to believe that the enormous magnitudes of the constants in Wertheim's equations have any physiological significance whatever.

The writers have replotted a number of Wertheim's series of measurements for the extensibility of muscle and nerve with logarithms of the stress as abscissae and extensions as ordinates, and three of them are shown in Fig. 1. The data from which they are plotted are reproduced in Table I. The letters

TABLE I

ELASTICITY OF MUSCLES AND NERVES. MEASUREMENTS OF WERTHEIM

Tissue	Weight, gm.	log W	Extension, mm.
A. Nerve—Tibial Posterior	150	2.18	7.38
	300	2.48	13.23
	450	2.65	19.40
	600	2.78	25.20
	750	2.88	30.64
	900	2.95	35.91
	1050	3.02	36.91
B. Nerve—Tibial Posterior	100	2	10.25
	200	2.30	16.13
	300	2.48	20.91
	400	2.60	24.62
	500	2.70	28.74
	700	2.85	33.40
C. Muscle—Stemomastod (dog)	8.4	0.92	7.40
	16.8	1.23	15.18
	25.2	1.40	22.88
	33.9	1.53	30.82
	42.5	1.63	36.22
	51.1	1.71	41.99
	59.7	1.78	48.46

1. *For convenience in plotting in the same figure, the characteristics of the logs in C have been increased by 1.*
2. *The weight is expressed in grams per square millimetre of cross section of the tissue.*

A, B, and C on the graphs refer to corresponding letters in the table. The graphs consist of two or three rectilinear parts with abrupt changes of slope which are represented by the equation:

$$E = k \log W + c,$$

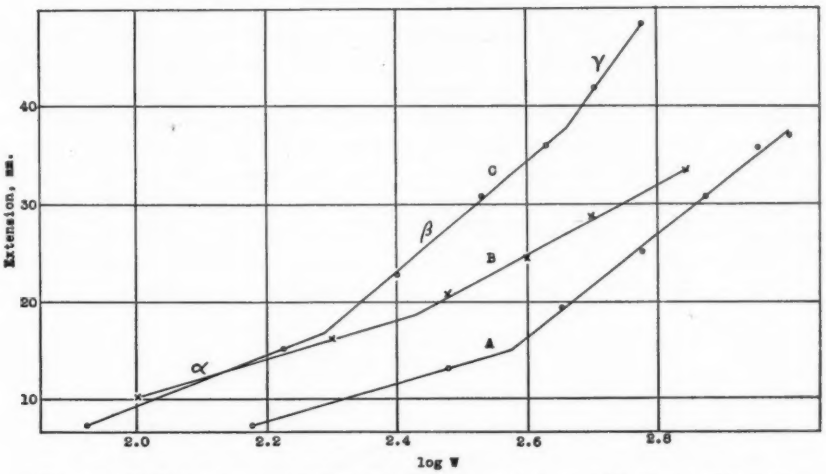

FIG. 1. *Wertheim's measurements of the elasticity of (A) nerve, (B) nerve, (C) muscle. The characteristics of log W for graph C have been increased by unity for convenience in plotting. Its real position is far to the left of the others.*

where E, replacing y in Wertheim's equation, is the extension, W, replacing X, is the stress, and k and c are constants, which have different numerical values in the different linear parts.

It may be remarked that Wertheim found the extensibility of bone to follow Hooke's law of elasticity for inorganic materials, which states that the elongation, or strain, is proportional to the stress, or, in symbols, $E = kW$.

Wertheim's measurements on any one tissue were few in number, especially for the smaller values of the stress. The lowest or α part of each graph therefore consists of only two points. The second or β parts, however, have from three to five points which satisfactorily demonstrate their rectilinear character. The third or γ part of one graph again has only two points. Since these graphs are found to be linear in form, Wertheim's proposed hyperbolic law of elasticity of organic tissues is evidently erroneous, and it can therefore be replaced by the simpler logarithmic law.

Wertheim measured the elasticity of human muscles (Sartorius) taken from subjects from 1 to 74 years of age, and from the measurements he computed the values of various constants:

Age	Value of a	Value of b	Coefficient of elasticity	Cohesion
1 (male)	607700	13832	1.271	0.070
21 (F)	1351875	8219	0.857	0.040
30 (M)	7960000	38860	0.352	0.026
74 (M)	14549333	23863	0.261	0.017

From these values it is clear that as age progresses both the elasticity and cohesion of muscles are greatly diminished. If the ages are plotted as abscissae and values of the coefficients of elasticity and of the cohesion as ordinates, the

shape of the curves indicates that the diminution follows an exponential law. This is confirmed, since exponential and logarithmic curves are closely related, by plotting logarithms of ages as abscissae, when the exponential curves become approximately straight lines. In the curves for the coefficient of elasticity, however, the second value, for the age of 21, departs widely from the graphs; this may be due to the fact that the subject was female, whereas the other three were male. Though the data are few and inconclusive, it may be tentatively assumed that the elasticity and cohesion of human muscles diminish in magnitude as the logarithms of the ages increase; or, in symbols,

$$E = -k \log A + c,$$

where E represents either the coefficient of elasticity or the cohesion, A the age of the subject, and k and c are constants. The negative sign indicates that the properties of the muscles diminish with age.

These measurements on human muscles are of a kind perhaps never repeated and the likelihood of confirmation or correction is probably not soon to be expected. It would seem, however, that the elasticity and cohesion of the muscles drop to half their value at about 25 years of age, or one-third of a lifetime. By extrapolation of the graphs to the zero base line, the interesting conclusion is suggested that could human life be prolonged to the age of 200 years, the elasticity of muscles would vanish, and in half a century more not even cohesion would remain. Since vital functions rest upon elasticity, it is at least clear that the rapid diminution of this property is one of the chief relentless foes of longevity.

Following the researches of Wertheim came the investigations of Marey (12, p. 284), which are quoted by Howell (10, p. 22), who showed that as the stress to which a living muscle was subjected was increased, the resulting extension diminished. His measurements, when plotted with the increments of elongation as ordinates and the stretching weights as abscissae, form a curve which is concave to the horizontal axis up to the limit of elasticity. When this critical value was exceeded, however, the muscle began to lengthen by increasing extensions for equal increments of weight up to the point of rupture.

In his treatise on physiology, Howell (10, p. 21) gives two diagrams in which the elasticity of a rubber band is compared with that of the gastrocnemius muscle of a frog for equal stretching forces. The rubber band, following Hooke's law of elasticity, shows equal extensions for equal increments of weight, while the muscle, under the same conditions of stretching, gives decreasing extensions. Since Howell's diagrams are drawn to scale, the writers measured, on that for the muscle, the elastic extensions corresponding to the nine weights used. They are given in Table II, and are plotted in two ways in Fig. 2. When extensions of the muscle are plotted against weights as abscissae, which are indicated on the upper part of the figure, the resulting broken line has a curved form. But when the elongations are plotted against the logarithms of the weights, the graph is perfectly straight, as indicated by

the continuous line, for eight of the points, while the ninth marks the beginning of a second linear part as in the graphs in Fig. 1. The equation representing the straight line is of the logarithmic type, precisely the same as before.

As part of a general plan of investigation of the responses to stimulation of different kinds of organs of the body which has been directed by one of the writers (Allen), Brisbin has conducted a series of researches on the elastic extensibility of muscles. His experiments were performed under conditions which, as far as possible, maintained the tissue under examination in its normal state. But in an investigation of this nature several factors may detrimentally influence the elasticity of the tissue. The complex chemical constitution of the fluids within the muscle substance undergoes alterations when the muscle is isolated which may affect its elasticity. Its properties are also influenced by changes in temperature as well as by the composition of the medium in which the muscle is immersed during the experiment.

TABLE II

ELASTICITY OF MUSCLES*

Weight, gm.	log *W*	Extension, mm.
20	1.30	0.19
23	1.36	0.36
26	1.42	0.50
29	1.46	0.63
32	1.51	0.75
35	1.54	0.86
38	1.58	0.96
41	1.61	1.05
44	1.64	1.16

**From "Text-book of Physiology" Howell. 12th ed. p. 21.*

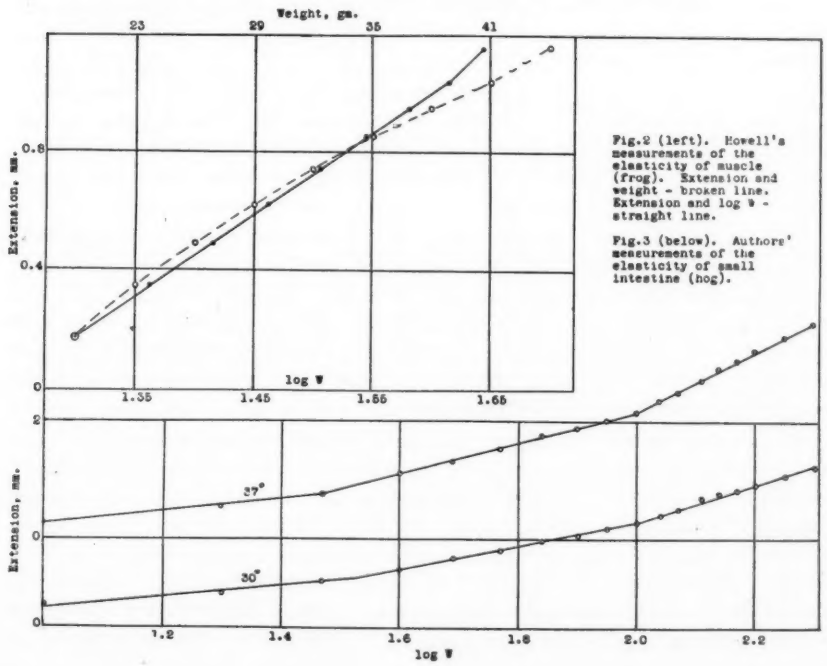

Fig.2 (left). Howell's measurements of the elasticity of muscle (frog). Extension and weight - broken line. Extension and log W - straight line.

Fig.3 (below). Authors' measurements of the elasticity of small intestine (hog).

It seems probable that the conditions governing a stretching muscle are similar to those prevailing during contraction. When a muscle shortens and doubtless also when it lengthens, the resting or equilibrium arrangement of the molecules or structural particles must rapidly change to other configurations appropriate to the new state. It was formerly concluded by Gasser and Hill (8) that the change of shape must be made against the hysteresis of the molecular system of the muscle and the viscosity of the muscle substance itself. An excited muscle is much less extensible than an unexcited one. In the former condition the new elastic state is produced and disappears more quickly than in the latter. A resting muscle when stretched and then released reaches equilibrium more rapidly than an active one, that is, an excited one was considered to be both more viscous and less extensible than one at rest. The basis of muscular contraction and extension was believed to consist of the two factors, elasticity and viscosity. In developing these views Levin and Wyman (11) concluded that the phenomena of muscular contraction could be accounted for on the assumption that the muscle is a complex system formed of two elements or mechanisms, one consisting of a free-elastic portion comparable to an undamped spring, and the other of a viscous-elastic portion comparable to a highly damped spring. The second portion was considered probably to be the contractile mechanism. Upon stimulation the latter elements were believed suddenly to change their elastic properties and thereupon to shorten and to stretch the free-elastic elements until a new condition of equilibrium is reached which is not directly proportional to the intensity of stimulation but follows an exponential law. Such a law is closely related to a logarithmic law. If the muscle consisted only of a structure with a free-elastic movement like a spring, as Weber assumed it to be, it might be expected when stretched to follow Hooke's law of elasticity. The presence of a viscous-elastic portion, or other complicating mechanism, however, indicates that the law of elasticity will likewise be complex, as the investigations of Wertheim and of the writers show it to be.

The most recent conclusions of Hill (9, p. 184) have radically altered these views by indicating that viscosity as a significant element in the process of muscular contraction must be entirely set aside. But the conclusion is maintained that "an active striated muscle is still a two-component system, consisting of an undamped purely elastic element in series with a contractile element governed by a characteristic equation" which, since it refers to the speed of contraction under stimulation, need not be considered here.

The measurements which are graphically shown in the figures of this communication, indicate that muscular elasticity, as far as elongation is concerned, is governed by a single logarithmic law. The fact that the graphs consist of several intersecting straight lines of different slopes may be interpreted as indicative of the existence of two components or processes which control the elasticity of muscles. The writers would prefer to consider the muscle not as two-component mechanisms, but as a single contractile-elastic system governed by two processes, one of which tends to enhance or facilitate

and the other to reduce or partially inhibit the elastic response to stretching or contracting forces. In physical terms these conditions may be thus stated: as the stress on a muscle is uniformly increased, the strain is not proportional to it according to Hooke's law of elasticity, but it varies as if it were controlled by two opposing processes, the ratio of their magnitudes changing at certain critical values of the stress which are those where the slopes of the graphs abruptly change. The nature of these controlling processes, which must be inherent in the muscle substance itself, cannot yet be suggested.

A somewhat analogous idea (Saunderson) was advanced many years ago that "the excitatory process in a muscle is made up of two antagonistic component processes, one of which is associated with shortening the other with relaxation". The possibility has also been suggested (J. von Kries, 1892) that a muscle is re-excited by the very effort which it makes in contracting or striving to contract.

While the most recent work has been undertaken from the point of view of contraction, it seemed appropriate to study more fully the process of extension also. For this purpose the following experimental procedure was devised. A light celluloid cylinder, containing a normal saline solution in which the muscle preparation or other elastic tissue was immersed, was fixed in position on a massive stand. The ends of the muscle were held firmly without tearing in aluminium clamps, the upper of which was attached to a rigid support on the stand and the lower to a fine steel rod which passed freely through a hole in the base of the cylinder. The aperture was made water-tight by a large drop of medium grade oil which offered no resistance to the movement of the rod. The lower end of the rod carried a light scale-pan on which weights were placed to stretch the muscle. The extension of the muscle was measured with a micrometer microscope, reading to 0.005 mm., by observing the sharp point of a fine steel needle affixed horizontally to the base of the scale-pan.

With this apparatus two series of measurements were obtained on the elasticity of pieces of the small intestine of the hog at temperatures of 30° and 37° C. The data are given in Table III, and they are plotted as before in

TABLE III

ELASTICITY OF MUSCLES. SMALL INTESTINE (HOG)

Weight, gm.	log W	Extension mm. 30° C.	Extension mm. 37° C.
10	1	0.40	0.28
20	1.30	0.57	0.55
30	1.48	0.79	0.80
40	1.60	1.00	1.14
50	1.70	1.20	1.34
60	1.78	1.33	1.55
70	1.85	1.47	1.77
80	1.90	1.58	1.90
90	1.95	1.68	2.02
100	2	1.80	2.15
110	2.04	1.92	2.34
120	2.08	2.05	2.50
130	2.11	2.20	2.70
140	2.15	2.26	2.90
150	2.18	2.33	3.02
160	2.20	2.42	3.18
180	2.26	2.57	3.44
200	2.30	2.74	3.65

Fig. 3, in conjunction with Fig. 2. Each graph consists of three linear parts which conform to the logarithmic law of elasticity. The parts of the graph for 37° are more sharply differentiated than those for the lower temperature.

In arranging an experiment with the same apparatus on the gastrocnemius muscle of a frog, the following procedure was adopted. After pithing the specimen from which the muscle was to be taken, a short time was allowed to elapse before the muscle was removed, so as to permit any condition of shock due to the operation to subside. After removal the muscle was placed firmly between the clamps, and an initial weight of 20 gm. was placed in the scale-pan which was allowed to act upon the muscle for two minutes before measurements were taken. The microscope was focused on the sharp point of the needle on the scale-pan and the zero reading made. Additional weights of 10 gm. at a time up to 200 gm. were added at intervals of one minute, and the corresponding extensions of the muscle were measured by means of the micrometer. The temperature of the saline bath was maintained approximately constant within 1° C. while a series of readings was taken.

It may be remarked that in these experiments various initial weights were sometimes employed, but they were found to have no observable effect upon the elastic property of the muscles. The time during which the stress acted upon the muscle before the reading of its extension was made also appeared to be devoid of influence upon the character of its extensibility.

A group of five series of measurements on the gastrocnemius muscle was obtained, the data for which are given in Table IV and plotted in Fig. 4,

TABLE IV

ELASTICITY OF MUSCLES. GASTROCNEMIUS MUSCLE (FROG)

Weight, gm.	log W	Extension mm. 12° C.	Extension mm. 17° C.	Extension mm. 26° C.	Extension mm. 30° C.	Extension mm. 35° C.
10	1	0.25	0.18	0.35	0.30	0.19
20	1.30	0.50	0.42	0.67	0.57	0.44
30	1.48	0.75	0.73	1.00	0.80	0.75
40	1.60	1.02	0.92	1.22	1.37	0.91
50	1.70	1.27	1.08	1.52	1.70	1.10
60	1.78	1.47	1.25	1.77	1.95	1.25
70	1.85	1.58	1.43	2.00	2.20	1.37
80	1.90	1.70	1.52	2.22	2.47	1.51
90	1.95	1.88	1.61	2.45	2.73	1.66
100	2	2.00	1.72	2.67	2.90	1.75
110	2.04	2.13	1.83	2.85	3.10	1.83
120	2.08	2.25	1.91	3.00	3.30	1.90
130	2.11	2.36	2.00	3.14	3.47	2.01
140	2.15	2.43	2.08	3.36	3.72	2.08
150	2.18	2.57	2.14	3.50	3.87	2.17
160	2.20	2.62	2.24	3.62	4.12	2.25
170	2.23	—	—	—	4.30	—
180	2.26	2.78	2.35	3.84	—	2.36
190	2.28	—	—	—	4.52	—
200	2.30	2.90	2.44	4.05	—	2.50
210	2.32	—	—	—	4.80	—

with total extensions as ordinates and logarithms of weights as abscissae. Each series was taken with a different muscle and at a different temperature ranging from 12° to 35° C. The graphs are plotted to the same scale, but, to afford comparison without confusion, the ordinates for four of them are

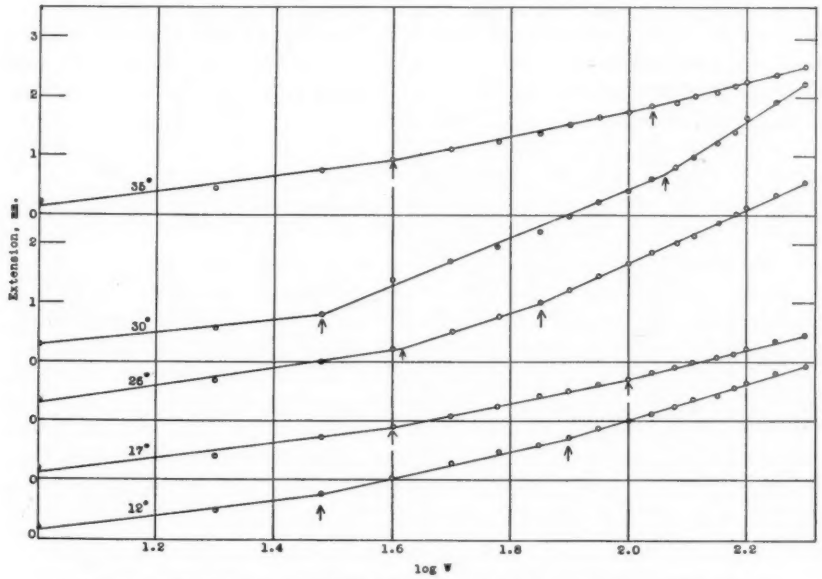

FIG. 4. *Elasticity of gastrocnemius muscle of frog at various temperatures.*

displaced upwards as indicated by the zero marks. Each graph consists of three linear parts which conform to the equation:

$$E = k \log W + c,$$

where E is the extension of the muscle produced by the weight W, and k and c are constants, which differ in numerical value for each part.

The influence of temperature upon the degree of elasticity is clearly shown, the graph for 30° having the best defined character as regards its linear parts.

From the positions of the intersection points of the parts of the graphs, it will be noticed that as the temperature of the muscle rises from 12° to 26°, it maintains the uniformity of its elastic properties for increasingly large stresses. At 30° this progression is reversed for the first point but not for the second. At 35° the graph approaches a straight line throughout its length; this indicates almost complete uniformity of elasticity for all values of the stress.

In the contraction of isolated muscles the temperature has a marked effect. The gastrocnemius muscle of the frog loses its irritability at or slightly below 0° C., a maximum contraction is obtained at from 5° to 9° C., while a further

rise in temperature to 15° or 18° causes a decrease in contraction. Beyond this point the contraction again increases to a second maximum at from 26° to 30°. A still further rise in temperature causes a diminution of contraction with a loss of irritability at 37° C.

In the present experiments on the stretching of muscles it was found that for temperatures ranging from 26° to 30°, the extension was from 3.4 to 6.05 mm.; for temperatures above 30° the extension fell to 2.5 mm., that is, a decrease in extension was shown. For temperatures from 12° to 17° the extension ranged from 2.44 to 2.9 mm., that is, a decrease in extension again occurs. The elasticity of the muscle at temperatures of 5° and 9° was also measured in this series of experiments, but the graphs are not given here. The extension was found to reach its first maximum value between these temperatures. It appears, therefore, that the relation between temperature and contraction applies also to temperature and extension.

During the summer of 1937 one of the writers (Brisbin) was enabled to continue the investigation at the Marine Biological Station, Wood's Hole, Mass., U.S.A., where he used the muscles of *Cancer irroratus* (Rock Crab), of *Callinectes sapidus* (Blue Crab) and of *Homarus americanus* (Lobster). In each case either the first or second pereiopodal or walking muscles were selected for the experiments on elasticity, the corresponding muscle in each species being always selected. A different specimen was used for each temperature which varied from 4° C. to 35° C. The measurements are given in Tables V, VI, and VII, and are plotted respectively in Figs. 5, 6, and 7.

TABLE V

ELASTICITY OF MUSCLES. *Cancer irroratus* (ROCK CRAB)

Weight, gm.	log *W*	Extension mm. 4° C.	Extension mm. 8° C.	Extension mm. 12° C.	Extension mm. 16° C.	Extension mm. 20° C.	Extension mm. 23° C.	Extension mm. 27° C.	Extension mm. 29° C.	Extension mm. 35° C.
20	1.30	0.51	0.85	—	0.69	0.33	0.65	0.25	1.10	0.82
30	1.48	0.82	1.40	0.68	1.03	0.58	0.80	0.77	1.55	1.27
40	1.60	1.04	1.90	1.07	1.40	0.90	1.05	1.10	1.90	1.42
50	1.70	1.38	2.15	1.50	1.63	1.05	1.11	1.25	1.96	1.60
60	1.78	1.67	2.55	1.77	1.86	1.23	1.20	1.45	2.11	1.75
70	1.85	1.89	2.95	1.93	2.11	1.29	1.20	1.50	2.21	1.82
80	1.90	2.09	3.07	2.05	2.36	1.33	1.40	1.79	2.40	1.90
90	1.95	2.25	3.35	2.27	2.49	1.38	1.57	1.83	2.57	2.06
100	2	2.45	3.55	2.53	2.65	1.40	1.64	2.04	2.75	2.12
110	2.04	2.60	3.76	2.80	2.78	1.49	1.75	2.08	2.85	2.20
120	2.08	2.76	3.94	3.01	—	1.61	1.84	2.27	2.92	2.26
130	2.11	2.89	—	—	3.08	—	1.91	2.34		2.32
140	2.15	3.01	4.05	3.23	—	1.78	2.02			2.34
150	2.18		—	—	3.52	—	2.06			Rupture
160	2.20		4.22	3.57	—	1.97	Rupture			
170	2.23		—	—	3.80					
180	2.26		4.47	3.80	—					
190	2.28		—		4.05					
200	2.30		4.53							
220	2.34		4.72							
240	2.38		4.95							
260	2.41		5.21							

In every case the total extension is plotted and not merely the increment of length for each additional weight. Increments, if desired, are easily obtained by subtracting successive values in the tables. It may be remarked that the same apparatus previously employed was used in the manner described above.

In Figs. 5, 6, and 7, the graphs are all plotted to the same vertical and horizontal scales. But in order to exhibit without confusion in the same figure the group obtained with each species of muscle at the different temperatures, the individual graphs are displaced vertically as in drawing Fig. 4. Though all zeros are not indicated on the figure, each graph has a separate zero value.

In Fig. 5 are shown nine graphs for the elasticity of muscles of as many specimens of Rock Crab at the different temperatures indicated. The initial weight was 10 gm., except for the temperatures 12° and 20°, where it was 20 gm., and the time elapsing after the weight was added and before the reading was taken was 1 min., except for 4° where it was 1.5 min., for 27° where it was 0.5 min., and for 20° where it was 2 min. The graphs consist of from two to four linear parts which conform to the logarithmic law of elasticity. The values of the initial weight and time intervals evidently have no apparent influence upon the form of the graph. All the measure-

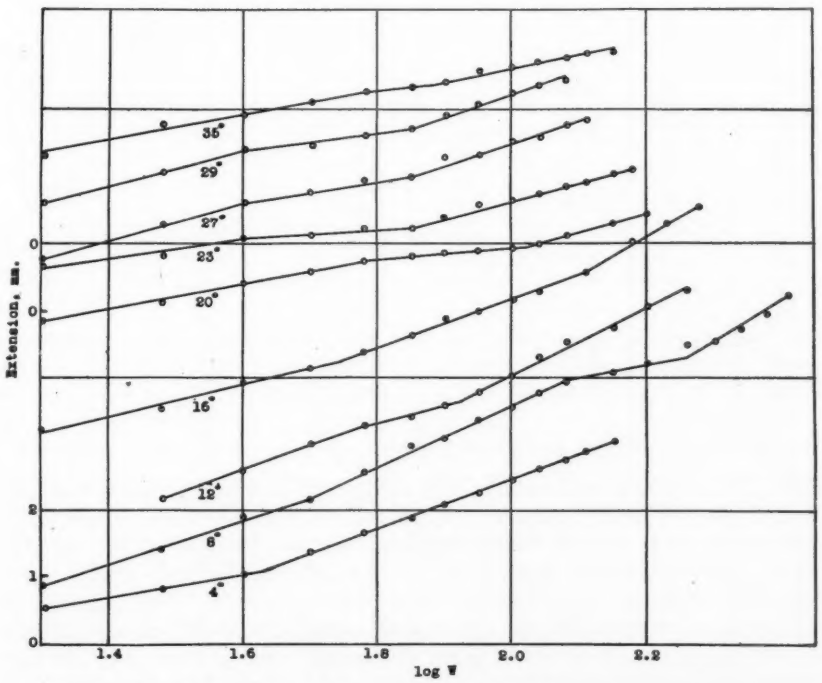

FIG. 5. *Elasticity of pereiopodal muscles of Rock Crab at various temperatures.*

ments lie on the graphs with remarkable precision. For in this and in the following two figures no point is away from the graph by an amount exceeding the very small quantity of 0.2 mm. By a comparison of the extensions for stresses of 140 gm. in Table V, it is seen that the value for 8° is the largest and that for 20° is the smallest. The extension rises to a maximum at 8° C. falls to a minimum at 20°, rises to a second but smaller maximum at 29°,

TABLE VI

ELASTICITY OF MUSCLES. *Callinectes sapidus* (BLUE CRAB)

Weight, gm.	log W	Extension mm. 7° C.	Extension mm. 14° C.	Extension mm. 22° C.	Extension mm. 27° C.	Extension mm. 30° C.	Extension mm. 34° C.
20	1.30	0.95	—	0.78	—	1.36	—
30	1.48	1.69	0.36	1.35	0.96	2.30	0.50
40	1.60	2.14	0.64	1.65	1.60	2.47	0.76
50	1.70	2.58	0.78	1.90	1.98	2.65	1.12
60	1.78	2.82	0.98	2.08	2.31	2.75	1.35
70	1.85	3.02	1.19	2.48	2.54	2.92	1.69
80	1.90	3.27	1.42	2.71	2.66	3.05	1.88
90	1.95	3.49	1.60	2.93	2.79	3.33	2.10
100	2	3.62	1.76	3.27	2.95	3.55	2.34
110	2.04	3.95	1.84	3.50	3.22	3.78	2.52
120	2.08	—	1.93	3.62	3.39	3.94	2.62
130	2.11	4.15	—	—	—	—	—
140	2.15	—	2.14	3.80	3.71	4.12	2.73
150	2.18	4.41	—	—	—	—	—
160	2.20	—	2.34	3.95	4.11	4.35	2.87
170	2.23	4.64	—	—	—	—	—
180	2.26	—	2.50	4.12	4.42	4.61	3.02
190	2.28	4.89	—	—	—	—	—
200	2.30	—	2.78	4.30	4.74	4.75	3.32
210	2.32	5.18	—	—	—	—	—
220	2.34	—	2.93	4.45	4.97	4.90	3.61
240	2.38	5.39	3.10	4.62	—	5.10	3.88
250	2.40	—	—	—	5.18	—	—
260	2.41	—	3.27	4.84	—	5.35	4.23
270	2.43	5.50	—	—	—	—	—
280	2.45	—	3.41	—	5.48	5.51	4.40
290	2.46	—	—	5.06	—	—	—
300	2.48	—	3.58	—	—	—	—
310	2.49	—		—	5.75	—	4.75
320	2.51	5.80		5.34	—	—	
330	2.52	—		—	—	5.92	
370	2.57	6.08		5.82	—	—	
380	2.58	—				6.28	

and again falls to a minimum at 35°, the graph for which is nearly a single straight line. While a different muscle was used at each temperature, it is probable at least that at 8° the elastic properties of muscle of this species reach their most pronounced character. This temperature is probably near that of the water in which the crab lives. It is noteworthy that with two of these muscles, which were used at temperatures of 23° and 35°, the logarithmic law of elasticity held up to the point of rupture. In no other case was the point of rupture attained.

In Fig. 6 are shown six graphs for measurements of the elasticity of the muscles of the Blue Crab. These also in all cases conform to the logarithmic law of elasticity. For the same temperatures they differ in shape from those in the preceding figure. The graph for 7° is almost a single straight line, while that for 22° has the most pronounced character as far as the number and distinctness of the linear parts show. In half of the graphs the initial weight

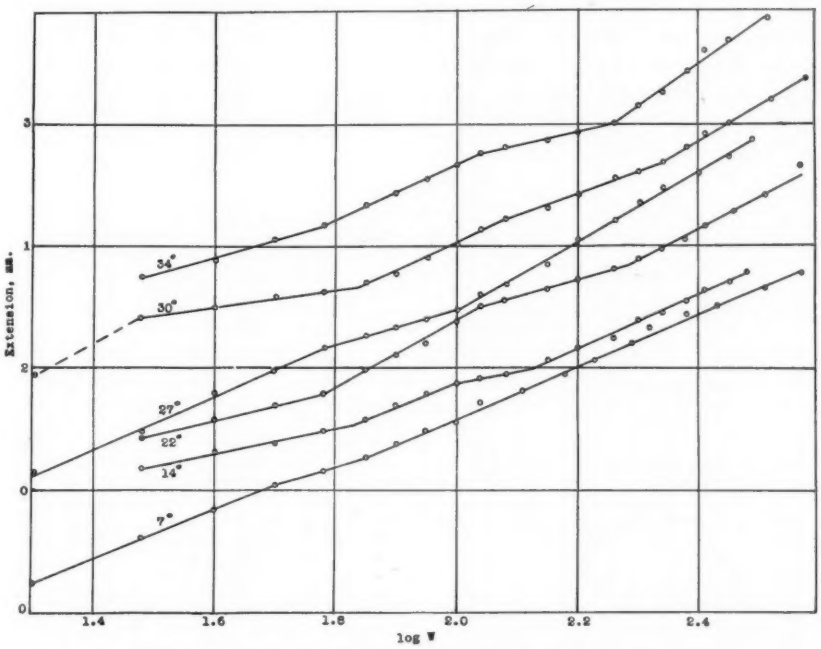

FIG. 6. *Elasticity of pereiopodal muscles of Blue Crab.*

was 10 gm. and in the remainder 20 gm., and the time elapsing between successive readings, after each additional stretching weight was applied, was either 1 or 1.5 min., and the increments of weight were 10 gm. up to stresses of 120 gm. Beyond this value the increments of stress were increased to 20 gm. up to 240 gm. and the time intervals were two minutes; for stresses in excess of 240 gm. the increments, as the table shows, were 30 gm., and in some cases, 50 gm., with slightly increased time intervals. None of these variations, however, show any want of conformity with the logarithmic law of elasticity. From the corresponding values in the table it appears that the extension of muscles in this species of crab is a maximum at 7°, a minimum at 14°, rises gradually to a second maximum at 30°, and declines towards a minimum again at 34°. This characteristic behaviour of the muscles of the Blue Crab is parallel with that of the Rock Crab, though the number of temperatures

upon which these conclusions are based is smaller in the former than in the latter case.

In Fig. 7 are shown nine graphs for measurements of the elasticity of the muscles of the Lobster. In all cases again they conform to the logarithmic law of elasticity, while the number of linear parts in the graphs varies from two to three. The graph for 10° is almost a single straight line and that for 22° is nearly so. In seven of the series of measurements the initial weight was 20 gm., and in the three remaining, for temperatures of 4°, 22°, and 30°, it was 10 gm. The time interval between readings while the weight was acting was generally 1.5 min., increasing to 2.5 min. when the increment of stress was increased to 20 gm. The corresponding values in Table VII show again a maximum extension of the muscles at 8°, a second maximum at 17°, and a third at 26°.

TABLE VII

ELASTICITY OF MUSCLES. *Homarus americanus* (LOBSTER)

Weight, gm.	log *W*	Extension mm. 4° C.	Extension mm. 8° C.	Extension mm. 10° C.	Extension mm. 12° C.	Extension mm. 17° C.	Extension mm. 22° C.	Extension mm. 26° C.	Extension mm. 27° C.	Extension mm. 30° C.	Extension mm. 35° C.
20	1.30	0.42	—	—	—	—	0.41	—	—	0.61	—
30	1.48	0.93	0.52	0.35	0.40	0.18	0.84	0.37	0.35	1.07	0.18
40	1.60	1.30	0.98	0.74	0.65	0.34	1.28	0.82	0.75	1.56	0.34
50	1.70	1.60	1.37	1.10	0.97	0.75	1.60	1.20	1.12	1.87	0.44
60	1.78	1.81	1.70	1.40	1.45	1.13	1.81	1.52	1.35	2.05	0.60
70	1.85	2.19	2.05	1.56	1.73	1.65	2.08	1.86	1.65	2.21	0.75
80	1.90	2.41	2.30	1.82	1.95	1.85	2.23	2.09	1.82	2.42	1.04
90	1.95	2.67	2.50	2.00	2.10	2.12	2.42	2.39	2.09	2.67	1.45
100	2	2.80	2.74	2.17	2.37	2.48	2.60	2.61	2.37	2.86	1.62
110	2.04	2.93	2.98	2.27	2.55	2.70	2.79	2.87	2.61	3.02	1.81
120	2.08	—	3.07	2.43	2.72	2.98	—	3.09	2.78	—	1.96
130	2.11	3.20	—	—	—	—	2.95	—	—	3.28	—
140	2.15	—	3.30	2.65	2.90	3.30	—	3.35	3.10	—	2.24
150	2.18	3.37	—	—	—	—	3.13	—	—	3.59	—
160	2.20	—	3.42	2.80	3.10	3.52	—	3.62	3.36	—	2.47
170	2.23	3.61	—	—	—	—	3.37	—	—	3.77	—
180	2.26		3.59	3.01	3.37	3.78	—	3.91	3.71	—	2.80
190	2.28		—	—	—	—	3.51			3.95	—
200	2.30		3.72	3.22	3.42	3.98				—	3.02
210	2.32			—	—	—				4.11	
220	2.34			3.37	3.66	4.32					

Without exception the 35 graphs, for three different kinds of tissues, in this communication, as well as a number not herein contained, conform to the logarithmic law of physiological elasticity. Whatever may be the factors in the complex constitution of muscles that combine to give them their elasticity, it invariably follows a definite mathematical law. When it is remembered that an error in the measurement of the extension of a muscle of 0.1 mm. throws a point perceptibly off from the straight line in the graph, and that no point has a greater variation than 0.2 mm., it will be realized how precise is the conformity to the law. The presence of several linear parts in each

graph shows also that muscular elasticity has not the same constants at all extensions or stresses, and that temperature modifies the elastic properties and constants without, however, destroying or changing the law. In its elastic properties muscular tissue clearly behaves much differently from inorganic materials which follow Hooke's simple law. It is quite possible that

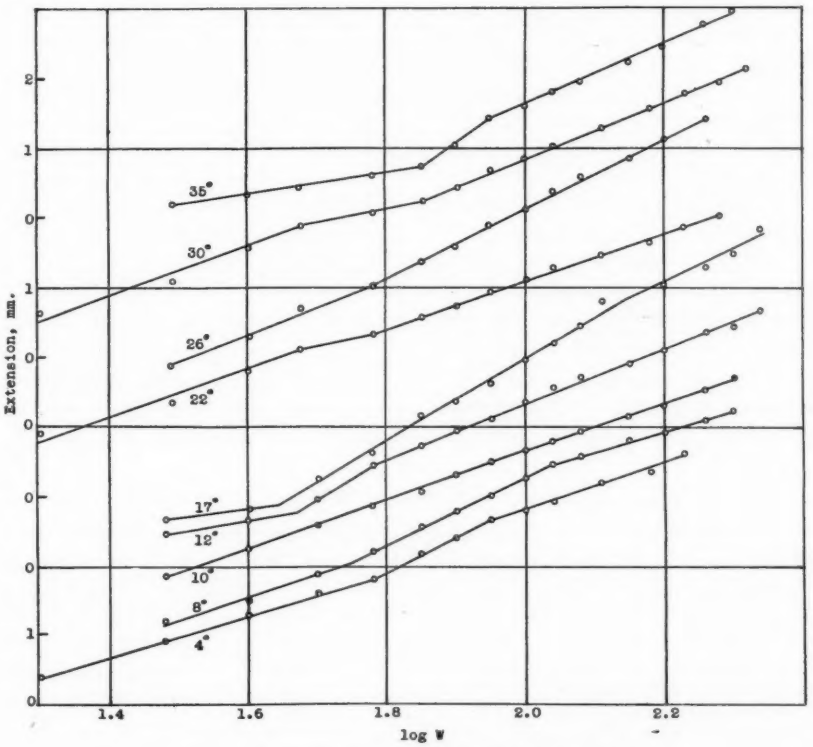

FIG. 7. *Elasticity of pereiopodal muscles of lobster.*

the logarithmic function enters the law of physiological elasticity because of the fact that a muscle is neither homogeneous nor isotropic in structure like a wire, but is composed of large numbers of fibres, each of which has contractility as well as elasticity. It is probable that each muscle fibre also obeys the same law of physiological elasticity since it likewise has a very complex structure. The logarithmic law of elasticity of muscles has the same form as the law of response to stimulation which has been found by Ferry (7) and by Porter (13) in vision, by Allen and O'Donoghue (5) in the post-contraction of muscles, by Allen (2) and his associates in the secretion of saliva, in the responses of the senses of hearing (1), taste (6) and touch (4), and in the processes of learning and relearning (3). Fundamentally it is similar to

Fechner's law connecting sensation and intensity of stimulation. It seems to be the characteristic mode of response for all activities of the organism where reactions to stimulation are involved.

It has generally been found that the elongations of a muscle under a stretching force gradually diminish in magnitude as the stress increases. This behaviour, indeed, is necessary for the effective working of muscles. It will be noticed in Tables V, VI, and VII that the elongations somewhat rapidly diminish towards fairly constant values, though in only two specimens of muscles (Table V) was the stress carried to the point of rupture of the muscles. In these cases the initial elongations for a stress of 10 gm. were 0.15 mm. and 0.45 mm.; with the former the elongation for an increase from 140 to 150 gm. fell to only 0.04 mm., and with the latter it was 0.02 mm. This is in accordance with other findings. In Table VI the measurements are shown for stresses up to 370 gm. In one case, at 7° C., the initial elongation for 10 gm. was 0.74 mm.; while for the last increment of 50 gm. it was 0.28 mm., which represents a lengthening of about 0.06 mm. for 10 gm. At 22° C. the corresponding elongations were 0.57 mm. and about 0.09 mm., and at 30° C. they were 0.94 mm. and 0.07 mm.

It may be concluded, therefore, that if the stresses had been sufficiently increased in all the experiments, there would have been found the conformity with the elastic behaviour of muscles which has been generally observed.

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THE ALKALOIDS OF FUMARIACEOUS PLANTS

XXI. *CORYDALIS LUTEA* (L.) DC.[1]

BY RICHARD H. F. MANSKE[2]

Abstract

Corydalis lutea (L.) DC. has yielded a total of seven alkaloids, four of which, namely: protopine, *l*-tetrahydro-palmatine, *l*-isocorypalmine, and isocorydine, are well known from other sources. The occurrence of the last, unaccompanied by corydine, is unique thus far. The name *stylopine* is retained for one of the alkaloids. On racemization it yields *dl*-tetrahydro-coptisine. *Ochrobirine* (alkaloid F14), one of the constituents, contains an esterifiable non-phenolic hydroxyl group, and the suggestion is advanced that it may be 13-hydroxy-protopine. Finally, a new non-phenolic alkaloid for which the name *luteanine* (alkaloid F44) is proposed, was found. It is isomeric with cularine, $C_{20}H_{23}O_4N$, and, like the latter, contains three methoxyl groups and an indifferent oxygen atom. It is pointed out that the nature of the chemical constituents, in this case alkaloids, offers a possible means of determining interrelations within a family. The close relation between *C. lutea*, *C. claviculata*, and *C. ochroleuca*, which has been proposed on morphological grounds, is not evidenced in the alkaloid constituents.

It is becoming increasingly evident that the chemical examination of plants offers a means of resolving disputed points of taxonomy. There are two important obstacles to classification based on morphology alone. In limiting cases, difficulties arise in closely related species, and botanists have no generally accepted criteria that would serve to allocate specificity to plants that are frequently regarded as varieties of a given species. In a previous communication the author has adduced evidence which, in his opinion, is sufficient to warrant the deduction that *C. micrantha* is not to be regarded as a varietal form of *C. aurea*. Similarly, *C. crystallina*, on the basis of chemical examination, is regarded as more closely allied to *C. sempervirens* than to *C. aurea*, of which it has been regarded as var. *crystallina* Torr. et Gray (10). A second moot point arises in attempts to subdivide a genus into sections and subsections. In this connection the three plants *Corydalis claviculata* (L.) DC., *C. lutea* (L.) DC., and *C. ochroleuca* Koch, have been grouped together in the section Stylotome Prantl., albeit, the first is differentiated from the others chiefly on account of ill-developed tendrils terminal on the leaves. *C. claviculata* has been under investigation for some time, but great difficulties have been encountered in the crystallization of most of the fractions. Nevertheless, the results thus far obtained do not justify the assumption of more than

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a remote relation. In fact, only two alkaloids, one of which is protopine, are contained in both plants. In the case of *C. ochroleuca** the relation to *C. lutea* is admittedly close. Of a total of eleven alkaloids in both plants, four are common constituents (protopine, ochrobirine (F14), *l*-isocorypalmine, and stylopine). Nevertheless, such typical alkaloids as isocorydine (*C. lutea*) and bicuculline (*C. ochroleuca*) serve to differentiate rather sharply two species that occasionally grow side by side but apparently do not hybridize. It is pertinent to note here that, while both the aporphine and phthalide-isoquinoline bases are widely distributed, no case is as yet known in which both types occur in the same plant, and a general system of classification based upon such considerations may well bear a close relation to a natural one. A similar and strictly parallel case is found in the pair, *Dicentra canadensis* and *D. cucullaria* (4, 6). Aporphine alkaloids (corydine, isocorydine, and bulbocapnine) occur only in the former and phthalide-isoquinoline alkaloids (bicuculline and corlumine) occur only in the latter. Nevertheless both have been relegated to the section Cucullaria Raf.** It is significant that the widespread protoberberine alkaloids are lacking in the above two species of *Dicentra* but occur in diverse forms in the three species of *Corydalis* mentioned above.

In addition to the alkaloids already mentioned (protopine, ochrobirine, *l*-isocorypalmine, *l*-tetrahydro-palmatine, and isocorydine), *C. lutea* has yielded two alkaloids, one of which has been identified as stylopine, an alkaloid first isolated from *Stylophorum diphyllum* by Schlotterbeck and Watkins (11). The author prepared a specimen of stylopine from the same source. It melts at 202° C.† and a mixture with a specimen from *C. lutea* melting at 206° C. melted at 204° C. The difference in melting points of the two bases has been found to be due to the presence of an appreciable quantity of the *dl*-base in the higher melting form. Go (3) has made the suggestion that the *l*-tetrahydro-coptisine which he isolated from *C. ternata* is identical with stylopine, and this suggestion is now proved to be correct. In the interests of priority and simplicity it is proposed to retain the name stylopine. The partially racemic stylopine from *C. lutea* was oxidized with iodine to the quaternary iodide (coptisine iodide) and the latter reduced to the tetrahydrobase. It melted at 221° C. and proved to be identical with the *dl*-tetrahydrocoptisine obtained by the author from *Fumaria officinalis* (8). A mixture of the pure *dl*-base with stylopine melted rather indefinitely at 210 to 215° C.

The remaining base, now termed *luteanine* (F44), is isomeric with cularine, $C_{20}H_{23}O_4N$, and like the latter, contains three methoxyl groups and an indifferent fourth oxygen atom.

The presence of isocorydine in the plant under consideration is of interest in that it has hitherto been found only in two plants (2, 4) and then only in association with corydine. *Ochrobirine* is the name now given to alkaloid F14

* *See the following paper.*

** *It is of interest to note that Pursh (Fl. Amer. Sept. II, 462 (1814).) has suggested a new generic name, Perizomanthus, for Dicentra cucullaria.*

† *All melting points are corrected.*

first obtained from *C. sibirica* (5). It has been observed that it yields a basic crystalline mono-acetyl derivative; hence, one of the oxygen atoms is probably present in an aliphatic hydroxyl group. Since the colour reaction is that of the protopine alkaloids and since at least one example is on record in which a hydroxyl group is a substituent in the heterocyclic system (9), the tentative suggestion that ochrobirine is 13-hydroxy-protopine is an attractive one. Some confirmation of such a structure was obtained when it was observed that a small amount of cuprous oxide is formed when ochrobirine is boiled with Fehling's solution containing some alcohol to render it soluble.

With reference to *l*-isocorypalmine, it may now be stated with some certainty that the identification is correct. It was first encountered in *C. caseana* (7), and was termed casealutine (F32). Methylation yielded an alkaloid that has now been identified with *l*-tetrahydro-palmatine. The melting point *in vacuo* is 240° C. without appreciable decomposition, and this is the value recorded by Gadamer and co-workers (1).

Experimental

The material for the present investigation was grown in a local garden and collected in September when it was still in flower although some seed had ripened. Representative specimens were sent to the Royal Botanic Garden, Kew, England, for identification. The author is pleased to acknowledge his indebtedness to the Director, Sir Arthur Hill, and to Mr. H. W. Pugsley for their kind attention to this detail. There was available a total of 6.6 kilos of dried material of which the roots constituted only an insignificant portion.

The following is a summary of the isolated alkaloids and the fractions from which they were isolated.

Base hydrochlorides extracted from aqueous solution by means of chloroform—

BC—Non-phenolic bases,—*l*-tetrahydro-palmatine, *l*-stylopine, luteanine.
EC—Phenolic bases extracted from alkaline solution by means of ether,—isocorydine.
BCE and EEC—Phenolic bases precipitated by carbon dioxide,—*l*-isocorypalmine.

Base hydrochlorides not extracted from aqueous solution by means of chloroform.

BS—Non-phenolic bases,—protopine, ochrobirine.
BSE and EES—Phenolic bases precipitated by carbon dioxide,—(not crystallized).

Luteanine

The fraction (BC) was redissolved in dilute hydrochloric acid, the clear filtered solution basified with ammonia, and the liberated bases were extracted with ether. The extract was clarified by means of charcoal and evaporated somewhat; colourless stout prisms crystallized from the solution. As thus obtained the base melted at 178° C. It was recrystallized twice from ether, in which it is only sparingly soluble. *Luteanine* thus obtained melted at 183° C. Recrystallization from methanol yielded stout colourless prisms of

the same melting point. The yield was 0.09%. Found: C, 70.33, 70.40; H, 6.79, 6.78; N, 4.26, 4.20; OMe, 27.71, 27.63%. Calcd. for $C_{20}H_{23}O_4N$: C, 70.38; H, 6.75; N, 4.10; 3OMe, 27.27%.

l-Tetrahydro-palmatine and l-Stylopine

When the mother liquor from the first crop of luteanine was evaporated to a small volume a mixture of bases crystallized. The more soluble portion was removed by washing with ether. The residue consisted largely of luteanine. The extract was evaporated to a small volume and on cooling deposited *l*-tetrahydro-palmatine, which, either alone or in admixture with an authentic specimen, melted at 141° C. A further amount of the same base was obtained from the mother liquor as its sparingly soluble hydrochloride. A total of 0.2% was obtained. The aqueous mother liquor from the latter was basified with potassium hydroxide and the liberated bases were extracted with ether. Evaporation of the solvent yielded a mixture from which the readily soluble *l*-tetrahydro-palmatine was separated by extraction with methanol. The sparingly soluble residue was recrystallized twice from chloroform-methanol and obtained in pale yellow fine prisms melting at 206° C. When this base was admixed with a specimen of *l*-stylopine (m.p. 202° C.) prepared from *Stylophorum diphyllum*, the mixture melted at 204 to 205° C. $[\alpha]_D^{23} = -178°$ ($c = 0.8$ in chloroform). The yield was somewhat less than 0.01%. Found: C, 70.14, 70.14; H, 5.30, 5.36; N, 4.49, 4.63%; OMe negative. Calcd. for $C_{19}H_{17}O_4N$: C, 70.59; H, 5.26; N, 4.33%.

That the base in reality is a partially racemic *l*-stylopine was proved by completely racemizing a portion of it. For this purpose 0.2 gm. was dissolved in 100 cc. boiling ethanol containing 2 gm. sodium acetate. Iodine was added to the boiling solution until an excess was present. The mixture was cooled and the dark brown quaternary iodide (coptisine iodide) was filtered off and washed with ethanol. It was suspended in glacial acetic acid to which some hydrochloric acid had been added. Zinc dust was added to the boiling solution until the mixture was colourless. Water was added, the filtered solution basified with excess ammonia, and the liberated base extracted with ether. The ethereal solution was thoroughly washed with water and evaporated to dryness. The resinous base crystallized at once in contact with methanol. It was recrystallized from chloroform-methanol and the colourless fine needles thus obtained melted either alone or in admixture with a specimen of *dl*-tetrahydro-coptisine at 221° C.

Isocorydine

The fraction (EC), as obtained by ether extraction from the strongly alkaline solution, consisted of almost pure isocorydine. When recrystallized twice from hot methanol it was obtained in large pale yellow prisms melting sharply at 184° C., and admixture with an authentic specimen did not lower the melting point. Yield, 0.07%.

An examination of the mother liquor from the latter failed to reveal the presence of corydine, for which a special search was made. In view of the

sparing solubility of the hydrochloride of this base and the failure to obtain it, the conclusion that corydine is not present is a reasonable one.

l-Isocorypalmine

The fraction (EEC) crystallized with great facility in contact with methanol, and fraction (BCE) crystallized readily when its solution in chloroform was evaporated somewhat and treated with methanol. The bases from these fractions proved to be identical. Further purification was effected by recrystallization from chloroform. *l*-Isocorypalmine as thus obtained melted at 230° C. Gadamer, Späth, and Mosettig (1), who isolated the *d*-form of this base from *C. cava*, give the melting point as 239° C., presumably uncorrected *in vacuo*. The base here described melted at 240° C. *in vacuo*. The optical rotation is $[\alpha]_D^{27} = -303°$ ($c = 0.4$ in chloroform). In admixture with a specimen of the alkaloid previously described as casealutine (7) there was no observable depression of the melting point, either in an open melting point tube or *in vacuo*. The methyl ether proved to be identical with *l*-tetrahydropalmatine. The yield of *l*-isocorypalmine was 0.01%.

Protopine and Ochrobirine

The fraction (BS) consisted of only a small amount of bases. Nevertheless, the isolation of pure protopine in a yield of 0.02% was readily effected by crystallization from chloroform-methanol.

The mother liquor from the crystallization of the protopine was evaporated to dryness and the residue dissolved in dilute hydrochloric acid. The filtered solution was basified with potassium hydroxide and extracted with ether. The washed solution was freed from solvent and the residue dissolved in a small volume of methanol. A base crystallizing in fine colourless needles was thus obtained. It melted at 138 to 139° C. with the evolution of a gas. This is the behaviour of the methanolate of alkaloid F14 (K), first obtained from *C. sibirica* (5), and a mixture of the two melted at 139° C.

It has been found that this alkaloid, for which the name *ochrobirine* is proposed, can be obtained free from solvent of crystallization if it is recrystallized from dry benzene. It is then obtained in hard stout polyhedra that melt at 198° C. Specimens from both sources were obtained in this form and admixture of the two did not lower the melting point. The solvent-free base yielded the following analytical figures. Found: C, 64.65, 65.39, 65.30; H, 5.20, 5.11, 5.37; N, 3.99, 4.05%; OMe, negative. Calcd. for $C_{20}H_{19}O_6N$: C, 65.04; H, 5.15; N, 3.79%.

The analytical figures previously recorded are for the mono-methanolate, and they agree as well for $C_{20}H_{19}O_6N \cdot CH_3OH$ as for the formula given earlier.

When the non-solvated base is dissolved in a small volume of chloroform and the solution treated with methanol, the fine needles of the methanolate, melting not quite sharply at 139° C., are again obtained. In chloroform ($c = 0.4$) the optical rotation was $[\alpha]_D^{21} = +35.9°$.

Acetyl-ochrobirine

The non-solvated form of ochrobirine (0.1 gm.) was heated with acetic anhydride (0.6 gm.) on the steam bath for 60 min. The cooled mixture was diluted with water and, after the excess anhydride was hydrolyzed, sodium carbonate was added. The precipitated base was filtered off, washed, and dried. It was recrystallized from hot methanol, in which it is readily soluble. Fine colourless needles melting sharply at 177° C. were thus obtained. *Acetyl-ochrobirine* yields with sulphuric acid an orange coloured solution, which changes to pink, slowly at room temperature and rapidly on warming. Further heating yields a deep purple solution. Calcd. for $C_{22}H_{21}O_7N$: C, 64.23; H, 5.11; N, 3.41%. Found: C, 63.64, 63.62; H, 5.20, 5.35; N, 3.16, 3.24%.

An attempt to reduce ochrobirine with zinc amalgam and diluted hydrochloric acid yielded an isomeric base. It was isolated from the basified solution by extracting with ether and adding methanol to the greatly concentrated solution. When recrystallized from chloroform-methanol it was obtained in colourless prisms melting at 238° C. The colour reaction with sulphuric acid was the same as that of ochrobirine, and it is possible that the attempted reduction merely effected racemization. Found: C, 64.95; H, 5.19; N, 3.60%. Calcd. for $C_{20}H_{19}O_6N$: C, 65.04; H, 5.15; N, 3.79%.

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THE ALKALOIDS OF FUMARIACEOUS PLANTS

XXII. *CORYDALIS OCHROLEUCA* KOCH[1]

By Richard H. F. Manske[2]

Abstract

Eight alkaloids have been isolated from *Corydalis ochroleuca* Koch. Of these, six, namely, protopine, ochrobirine, *l*-tetrahydro-palmatine, bicuculline, *l*-corypalmine, and *l*-isocorypalmine, have been described from other sources. The last was the most abundant of the alkaloids in this plant, and was isolated in 0.11% yield of the dry weight. Two apparently new alkaloids have also been found. They are referred to as *alkaloid F45* ($C_{20}H_{19}O_8N$) and *alkaloid F46* ($C_{11}H_9O_2N \cdot \frac{1}{2}H_2O$). The former is phenolic and the latter contains a methylenedioxy group.

In a previous paper (2) the author pointed out that, on the basis of taxonomic classification, *Corydalis claviculata* (L.) DC., *C. lutea* (L.) DC., and *C. ochroleuca* Koch are regarded as closely related and therefore placed in one section, namely, Stylotome Prantl. It may be pointed out that, as the name indicates, *C. ochroleuca* can be distinguished from *C. lutea* by virtue of the fact that its flowers are white and yellow, whereas those of the latter are pure yellow. Closer examination reveals the fact that the axillary angles in *C. ochroleuca* are much more acute than those of *C. lutea*, which tend to approach right angles. These features are clearly shown in the accompanying plate, in which *C. claviculata* is included for comparison. In general aspect the last is obviously different from the others, but this is largely due to its more branched and climbing habit.

The chemical relation between *C. lutea* and *C. ochroleuca* has already been discussed, and the present paper deals with the alkaloids that have been isolated from the latter plant. Of a total of eight alkaloids only two appear to be new and are referred to as alkaloids F45 and F46. Both bases lack methoxyl groups and the former appears to be phenolic. Alkaloid F45 yields analytical figures in agreement with the empirical formula $C_{20}H_{19}O_8N$. In view of its solubility in bicarbonate solutions and insolubility in ether, it may be the hydroxy-acid form of a phthalide-isoquinoline alkaloid containing an additional hydroxyl group in the benzene ring. Alkaloid F46 is best represented by $C_{11}H_9O_2N \cdot \frac{1}{2}H_2O$. It is expected that more material will be available in the near future, and the further characterization of these alkaloids will then be attempted.

The remaining alkaloids, namely, *l*-tetrahydro-palmatine, bicuculline, *l*-corypalmine, *l*-isocorypalmine, protopine, and ochrobirine, have been frequently described and call for no special comment, except that this is the third recorded source of the last. Finally, at the risk of weary repetition, it is again pointed out that the chemical examinations reported in this series

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cannot be regarded as complete. Paucity of material and difficulties of crystallization are obstacles not immediately surmountable.

Experimental

There was available a total of 5.8 kg. of dried and ground material. The plants were grown in a local garden in a plot adjacent to that in which *C. lutea* was grown. Several specimens were sent to the Royal Botanic Garden, Kew, England, for identification, and the author records his indebtedness to Sir Arthur Hill, the Director, for his valuable aid.

The following is a summary of the alkaloids together with the fractions from which they were isolated.

Base hydrochlorides extracted from aqueous solution by means of chloroform—

BC—Non-phenolic bases,—*l*-tetrahydro-palmatine, bicuculline.
EC—Phenolic bases extracted from alkaline solution by means of ether,—*l*-isocorypalmine.
BCE and EEC—Phenolic bases precipitated by carbon dioxide,—*l*-corypalmine.
CEC—Phenolic bases extracted from the carbonated solution by means of chloroform,—alkaloid F45.

Base hydrochlorides not extracted from aqueous solution by means of chloroform—

BS—Non-phenolic bases,—protopine, ochrobirine.
ES—Phenolic bases extracted from alkaline solution by means of ether,—alkaloid F46.
BSE and EES—Phenolic bases precipitated by carbon dioxide,—*l*-isocorypalmine (trace).

Bicuculline and l-Tetrahydro-palmatine

A solution of fraction (BC) in methanol was partly neutralized with hydrochloric acid and treated with a little ether. A small amount of crystalline material separated from this mixture. After two recrystallizations from chloroform-methanol it was obtained in colourless prisms melting at 177° C.*, either alone or in admixture with a specimen of bicuculline. A portion was converted into the high melting form (m.p. 195° C.); admixture of this with bicuculline did not lower the melting point. The yield was 1.5 gm.

The filtrate from the bicuculline was diluted with water and freed from organic solvents on the steam bath. The filtered solution was basified with potassium hydroxide and the liberated base extracted with ether. The washed and concentrated extract deposited the hydrate of *l*-tetrahydro-palmatine on cooling. It melted with effervescence at 115° C. A portion was converted to the anhydrous form, which melted at 142° C. either alone or in admixture with an authentic specimen. The yield was 2.1 gm.

l-Isocorypalmine

During the extraction of the alkaline filtrate from fraction (BC) to obtain fraction (EC), small amounts of dilute hydrochloric acid were added to reduce the alkalinity. While the filtrate was still quite alkaline, a crystalline preci-

* *All melting points are corrected.*

Corydalis ochroleuca

Corydalis lutea

Corydalis claviculata

PLATE I

pitate virtually insoluble in ether separated from the mixture. It was filtered off, and, after washing and drying, it melted at 231° C. to a reddish-brown melt. It was recrystallized from a large volume of hot chloroform in which it is only sparingly soluble. It still melted at 231° C. *In vacuo* it melted more sharply at 240° C. Also, in admixture with specimens of *l*-isocorypalmine from *C. lutea* (2) and *C. caseana*, it melted at 240° C. *in vacuo*. The ether extract (EC) consisted largely of the same base. The total yield was 6.7 gm. (0.11%). *l*-Isocorypalmine is therefore the principal alkaloid in *C. ochroleuca*, which plant incidentally is by far the best source of this hitherto rare alkaloid.

l-Corypalmine

The fractions (BCE and EEC) in contact with methanol yielded a further small amount of *l*-isocorypalmine, which crystallized readily. The filtrate from this alkaloid was evaporated and the residue dissolved in dilute hydrochloric acid. The bases were regenerated from the filtered solution by means of ammonia and extracted with ether. The residue from the ether extract crystallized in contact with methanol. As thus obtained it melted at 227 to 228° C. and admixture with *l*-isocorypalmine lowered the melting point to 215° C. In admixture with *l*-corypalmine it melted at 228 to 229° C. With sulphuric acid it gave a series of colours indistinguishable from those of the latter. The yield was 0.07 gm.

Alkaloid F45

The aqueous carbonated solution from which fraction (EEC) had been obtained yielded to chloroform extraction a moderate amount of another alkaloid. This fraction, for which the designation (CEC) is now proposed, is of appreciable bulk in the case of only a few plants. In the present instance the residue from the chloroform extract could not be crystallized directly. It was dissolved in dilute hydrochloric acid and the filtered solution basified with ammonia. No immediate precipitate was formed. The slightly turbid solution was filtered and allowed to evaporate slowly. The crystalline base which separated in the course of several days was filtered off and washed with water. It was dissolved in chloroform and the solvent evaporated. Methanol was added and the remaining chloroform boiled off. The cautious addition of water yielded hard colourless prisms, which were filtered off and washed with the following liquids in the order given,—methanol, water, methanol, and ether. Alkaloid F45, as thus obtained, melted to a dark tar at 268° C. It dissolves in sulphuric acid to a greenish-yellow solution that becomes orange on gentle heating. Further heating changes the colour of the solution to brown and finally to olive, which colour remains on cooling. The yield was 0.1 gm. Found: C, 60.62, 60.60; H, 4.76, 4.77; N, 3.29, 3.30%; OMe, absent. Calcd. for $C_{20}H_{19}O_8N$: C, 59.85; H, 4.74; N, 3.49%.

Protopine and Ochrobirine

The fraction (BS) was dissolved in chloroform and the filtered solution (charcoal) evaporated to dryness. The residue was dissolved in dilute hydro-

chloric acid and the filtered solution basified with potassium hydroxide. The liberated base was extracted with ether and the extract evaporated to dryness. A methanolic solution of the residue was inoculated with a crystal of protopine. The base which then crystallized was virtually pure protopine (yield, 0.9 gm.).

The filtrate from the protopine deposited in the course of several days a crop of colourless elongated needles, which were dissolved in boiling methanol. Ochrobirine crystallized with great facility when the methanolic solution was evaporated to a small volume. It melted at 138 to 139° C. either alone or in admixture with a specimen of alkaloid F14 from *C. sibirica* (1). A portion was converted to the high melting form (m.p. 198° C.), and this had the properties of the base similarly obtained from the alkaloid from other sources. The yield was 0.3 gm.

Alkaloid F46

The fraction (ES) crystallized with great facility when the ether was distilled off. It was dissolved in chloroform and the solvent evaporated. Crystallization ensued almost at once when the amorphous residue was dissolved in hot methanol. The base was recrystallized again from chloroform-methanol; it then consisted of large pale yellow prisms that melt without appreciable decomposition at 227° C. It dissolved in sulphuric acid to yield a pale yellow solution; when the solution was warmed the yellow colour faded somewhat, and on further heating it only became brown. A test for the methylene-dioxy group with 80% sulphuric acid and phloroglucinol was strongly positive. It is not probable that alkaloid F46 is phenolic, as it would not dissolve in aqueous potassium hydroxide solution. The yield was 0.15 gm. Found: C, 66.22, 66.26; H, 5.23, 5.40; N, 7.18, 7.26%. OMe, negative. Calcd. for $C_{11}H_9O_2N \cdot \frac{1}{2}H_2O$: C, 67.35; H, 5.10; N, 7.17%.

As in all plants of the genera *Dicentra*, *Corydalis*, and *Fumaria* thus far investigated, fumaric acid was encountered.

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THE CORROSION OF IRON ELECTRODES BY A.C. IN AQUEOUS ELECTROLYTES[1]

By J. W. Shipley[2] and G. R. Finlay[3]

Abstract

The corrosion of iron electrodes when a.c. is used was found to be a function of the composition and concentration of the electrolyte and of arcing on the electrodes. No particularly corrosive effect could be attributed to the presence of chlorides, but sulphates were found to induce corrosion. Magnesium and calcium salts inhibited corrosion even in the presence of sulphates. The addition of a soluble magnesium salt to the feed water and the operation of the generator under pressure in order to prevent arcing are suggested as a means of minimizing corrosion of the electrodes in a boiler of the resistor type.

Introduction

The preparation of steam in electric boilers of the resistor type, in which iron electrodes, natural waters as electrolyte, and a.c. as the source of thermal energy, are used, is common practice for the generation of steam where hydroelectric power is available. A previous investigation by one of us (2) draws attention to the corrosion of the electrodes in relation to current density and arcing. The present investigation concerns the corrosion of iron electrodes in relation to the composition of the electrolyte when 60 cycle 110-volt current is used. This voltage is far below that employed in the production of steam, but is nevertheless sufficiently high to produce boiling, arcing, and gas formation, the important phenomena accompanying the generation of steam in an a-c. water resistor steam generator.

The generation of steam increases the natural salt content of the water until the lowering of the electrolytic resistance makes it desirable to "bleed" the generator and run off the water of relatively low resistance. A feed water from a river or lake may have a very low salt content, but owing to evaporation the salt content increases continuously.

Experimental

In the operation of a steam generator of this type, natural waters containing various salts in different concentrations are used. This investigation concerns the observed corrosion when a.c. and certain individual salts and salt mixtures, commonly found in natural waters, are used, the concentrations employed being those likely to be encountered in actual practice. The corrosive effect of some natural waters with a mixed salt content was also studied. Table I contains the results observed when electrodes of commercial soft iron wire, cleaned with fine emery, and of 0.102 cm. diameter and 2 to 2.5 cm. long, are submerged in the electrolyte designated, and submitted to the action of a 60 cycle, 107 to 115 volt, alternating current.

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Contribution from the Chemistry Department, University of Alberta, Edmonton, Canada.
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The loss of iron by corrosion was determined by one or more of the methods given below.

(1) Dissolving, in sulphuric acid, the particles loosened by corrosion, reducing and titrating with potassium permanganate.

(2) Determining the loss in weight of the electrodes.

(3) Drying the products of corrosion at 120° C., weighing, and calculating the iron content from the formula $Fe_3O_4 . H_2O$.

(4) Ascertaining the excess of hydrogen over that of oxygen in the evolved gases; when calculated to iron as Fe^{++}, this gave a measure of the corrosion.

The results listed in Table I were all computed from the analysis as in Method (1), except where otherwise indicated. The corrosion is calculated as though it were uniform over the surface of the electrode, and is expressed as loss of iron off the surface in centimetres per year of continuous use. The corrosion of the electrode in pitted areas would no doubt be much more rapid than that indicated by the results tabulated.

No relation between current density and corrosion could be established, as the current fluctuates violently as soon as bubbles of steam are generated

TABLE I

CORROSION OF IRON ELECTRODES BY A-C. ELECTROLYSIS

Using submerged electrodes 0.102 cm. in diameter and 2 or 2.5 cm. in length. Current; 60 cycle, 107 to 115 volts. Time of run, one hour. Temperature, the boiling point of the electrolyte

Electrolyte	Corrosion results Loss of iron off surface, in cm./year	Remarks
NaOH, *N*/10	6*, 5	Arcing in both cases
$NaHCO_3$, *N*/10	2, 6, 9	Foaming and no arcing, sludge formation
Na_2CO_3, *N*/10	12, 3, 5	Sludge formation, no arcing, foaming
NaCl, *N*/10	18, 15	No arcing
NaCl, *N*	325	Arcing
$CaCl_2$, *N*/10	6, 6, 4, 0	No arcing
$CaCl_2$, *N*	90	Arcing
$MgCl_2$, *N*/10	7, 3, 0, 15, 25	Arcing in last two runs
$MgCl_2$, 1.5 *N*	180	Arcing
$MgSO_4$, *N*/10	2, 2, 0	No arcing
$MgSO_4$, *N*	12	Arcing negligible
$CaSO_4$, sat'd	0	No arcing
Na_2HPO_4, M/4	12	Electrodes coated, no arcing
Na_2SO_4, *N*/10	80†, 135, 130*, 105, 125*, 105†°	Most of these values were also checked by measurement with micrometer. No arcing.
Na_2SO_4, *N*/20	130, 110°	No arcing
Na_2SO_4, *N*/30	85*	No arcing
Na_2SO_4, *N*/50	90 (45 at 82° C.)	No arcing
$FeCl_3$, *N*/10	163°†	pH = 1.8. No arcing
$FeSO_4$, *N*/10	35°†	pH = 3.8. No arcing
$KMnO_4$, *M*/100	Attack not serious	Permanganate partially reduced to MnO_2. No arcing

° *Method of analysis No. 2.*
† *Method of analysis No. 3.*
* *Method of analysis No. 4.*
All not marked were calculated from the determination of iron by Method No. 1.

on the electrodes, and the distribution of current on the electrodes becomes a function of the insulating effect of the bubbles. The size, continuity, and distribution of the bubbles on the electrodes is quite irregular and varies between the electrodes. Often all the steam is generated at one electrode. Arcing on the electrodes also causes a marked fluctuation in the current, the current invariably dropping when arcing begins.

Fig. 1, compiled from some of the data included in Table I, shows more strikingly the relative rates of corrosion of iron in 0.1 *N* solutions of the salts.

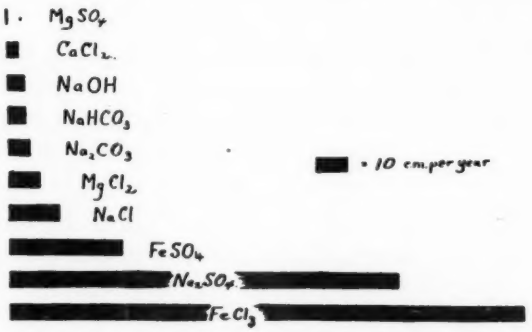

FIG. 1. *Corrosion of iron electrodes in N/10 electrolytes (a.c.)*

The figure is constructed from the average rate of corrosion in all the corresponding salt solutions.

The relative rate of corrosion was determined in some natural waters of high salt content, the concentration somewhat simulating that to be expected in an electric boiler before "bleeding" is resorted to. Five of the samples were from wells in Alberta, one was of water from a "muskeg", one from the North Saskatchewan River at Edmonton, and another a solution of "humic" or "ulmic" acid prepared synthetically from rotting moss (3). An analysis of some of these waters is given in Table II.

TABLE II

ANALYSIS OF WATERS (P.P.M.) USED IN THE CORROSION TESTS INCLUDED IN TABLE III

—	Well No. 1	Well No. 2	Well No. 3	Well No. 4	Well No. 5	Sask. River water, August
Total solids (after heating to 150° C.)	1710	1030	4954	1822	2006	199
Total hardness (Ca and Mg to $CaCO_3$)	800	500	500	20	20	152
SO_4^{--}	300	270	2300	995	400	25
Cl^-	143	24	140	77	28	4
Alkalinity (total CO_3^{--} calcd. to $CaCO_3$)	880	445	440	295	1150	110
Nature of alkalinity	Ca and Mg	Ca and Mg	Ca and Mg	Na 232, trace Ca	Na, no Mg. trace Ca	Ca and Mg
pH	8.9	7.2	8.5	8.4	9.2	8.1

The "muskeg" swamp water had a magnesium sulphate content of about 0.1 N and a pH of 6.3; the pH of the synthetic humic acid solution was 4.1.

Fig. 2 is compiled from the data in Table III.

To test whether the a-c. electrolysis of a chloride solution using iron electrodes might produce chlorine, hydrogen chloride, or hypochlorite, a series of determinations was made in which magnesium chloride was employed in concentrations varying from 0.1 to 1 *N* over a range of current densities.

TABLE III

CORROSION OF IRON ELECTRODES BY A-C. ELECTROLYSIS (CONDITIONS AS GIVEN IN TABLE I)

No arcing was observed during any of these determinations

Sample of water	Corrosion	pH	
	Loss of iron off surface in cm./year	Initial	After one hour
Humic acid	0, 0*	4.1	—
"Muskeg"	0, 2†	6.3	8.0
Sask. River	0, 0, 3	8.3	9.1
Well No. 1	1, 3	8.9	> 10
Well No. 2	14, 2	7.2	8.7
Well No. 3	25, 15, 35	8.5	9.3
Well No. 4	95, 150	8.4	> 10
Well No. 5	160, 115	9.2	10

* *Electrodes coated.* † *Magnesium sulphate, about 0.1 N.*

Arcing occurred, erratic at low, but steady at higher, current densities, but no evidence of free chlorine, hydrogen chloride, or hypochlorite was found in either the residual electrolyte or in the distillate. When arcing occurred, severe corrosion was observed with the formation of the black oxide of iron. As aluminium electrodes possess a low critical current density (2) in respect to gas evolution, these were substituted for the iron electrodes, and although hydrogen and oxygen were evolved copiously no chlorine was detected. Elec-

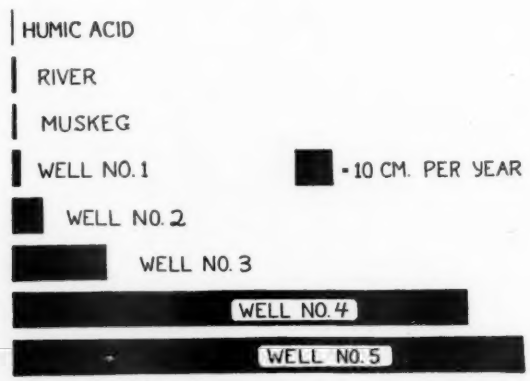

FIG. 2. *Corrosion penetration in iron electrodes—a-c. electrolysis in natural waters.*

trodes of No. 30 aluminium wire were completely corroded in three minutes. Before disintegration, the electrodes became covered with a white deposit of magnesium hydroxide, quite adherent to the electrodes, and gas evolution diminished. The pH of the electrolyte fell from 6.0 to 5.0. Gas production, principally of hydrogen and oxygen, occurred in all cases, with or without arcing, but more copiously with arcing. The excess of hydrogen over oxygen in the evolved gases gave a measure of the extent of the corrosion. Sodium hydroxide as electrolyte gave practically equivalent quantities of hydrogen and oxygen without corrosion, whereas sodium sulphate gave a large excess of hydrogen over oxygen, with a corresponding corrosion measured by the difference. Electrolytes containing calcium sulphate or magnesium sulphate evolved little gas, and the corrosion was slight. Carbonates and bicarbonates on electrolysis produced some carbon dioxide, and the pH rose from 8.5 to 10.0 whenever bicarbonate was present. Chlorides did not produce any appreciable amounts of chlorine or hydrogen chloride.

Protective Coatings

As electrolytes containing calcium and magnesium salts were observed to inhibit corrosion, tests were carried out to determine the practicability of adding substances to the electrolyte with the expectation that a measure of protection against corrosion (3) might be secured. "Water glass" was found to afford some protection when added to an electrolyte containing sulphate ions, but sludge formation and foaming were enhanced. Aluminium chloride promoted corrosion, foaming, and the production of sludge. Potassium dihydrogen phosphate inhibited corrosion in a sulphate-containing water, but, when the phosphate coated electrodes were used in the absence of phosphate, corrosion proceeded unimpeded. Apparently protection is afforded only if phosphate ions are present. Addition of lime gave no protection in an electrolyte containing sulphate ions, but calcium chloride did. A sludge of calcium sulphate was formed. Calcium chloride added to well waters Nos. 3, 4, and 5 proved to be protective unless arcing occurred. Magnesium chloride added to the well waters inhibited both the corrosion and arcing. A mixture of "water glass" and calcium or magnesium chloride was not found to be protective, and objectionable sludge formation occurred. Magnesium sulphate or chloride added to an electrolyte gave the best results, as no sludge formation followed. Sodium carbonate or sodium hydroxide did not inhibit corrosion in the presence of sulphate ions. Colloids such as glue and gelatin were ineffective.

Discussion

Reference to Tables I and III and Figs. 1 and 2 indicates that when a.c. is used there is a large difference in the rate of corrosion of an iron electrode depending on the nature of the electrolyte and the concentration. Both the cations and the anions are concerned. Production of an insoluble compound on the electrodes tends to protect the electrode from corrosion. Thus a film of calcium or magnesium hydroxide may be formed over the surface when the electrolyte contains these cations, for during the half-cycle when

hydrogen is being discharged on the electrode the solution in immediate contact with the electrode possesses an excess of hydroxyl ions, and the above mentioned insoluble hydroxides may be formed. During the second half-cycle, when the electrode becomes anodic, this film may not be completely reduced, and, as electrolysis proceeds, the layer will increase and become more protective, as the underlying iron is kept from contact with the electrolyte. This explanation is supported by the experimentally observed fact that, in solutions of calcium and magnesium salts, a.c. produces on the electrodes a coating resembling these hydroxides and certainly containing the respective cations.

The formation of such protective coatings would account for the low corrosive effect of the magnesium and calcium salt electrolytes shown in Table I and Fig. 1, and also for the relative position of the natural waters, as regards corrosion, given in Table III and Fig. 2. Those waters containing either or both of these alkaline earth metals are relatively non-corrosive.

The synthetic humic acid water, although of a pH of 4.1, proved to be non-corrosive. The electrodes were covered with a visible loose deposit, probably of a colloid collected by cataphoresis.

Sodium sulphate proved to be very corrosive. Natural waters containing sulphate and little or no calcium or magnesium were also very corrosive. Sodium chloride was not particularly corrosive as compared with the sulphate, but ferric chloride was the most corrosive electroyte used. The last-named electrolyte had a pH of 1.8 and thus was quite acid; at the temperature of boiling this condition no doubt made it very reactive with the iron and kept the electrodes clear of any protective deposit.

The effect of increase in concentration of salts in the electrolyte was in general to promote arcing and corrosion. Arcing, with its consequent high temperature and the rapid formation and collapse of steam bubbles, jars the electrodes and tends to break up any loosely adhering protective coating that might form. It also increases the local current density and thus promotes corrosion.

Sodium hydroxide electrolyte was non-corrosive even when arcing occurred. Electrolysis produces hydrogen and oxygen.

Arcing on the electrode was found to be very conducive to corrosion. Since arcing occurs across bubbles of gas and the suppression of such bubbles can be secured by operating the boiler under pressure, it is suggested that generators be operated at a pressure sufficient to prevent steam formation and that the hot water be allowed to vaporize under reduced pressure in a separate chamber. The suppression of bubble formation on the electrodes would also tend to give uniform current density distribution on the surface of the electrodes and thus distribute any unavoidable corrosion uniformly over the surface. This would tend to diminish pitting of the electrode.

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THE KINETICS OF THE DECOMPOSITION REACTIONS OF THE LOWER PARAFFINS

IV. THE ROLE OF FREE RADICALS IN THE DECOMPOSITION OF *n*-BUTANE[1]

By E. W. R. Steacie[2] and H. O. Folkins[3]

Abstract

An investigation has been made of the inhibition of free radical chain processes in the decomposition of *n*-butane by the addition of nitric oxide. The method was to initiate chains in butane at low temperatures by means of ethylene oxide, and then to investigate the efficiency of nitric oxide in suppressing these chains.

It was found that nitric oxide is not completely efficient as a chain breaker, inasmuch as sensitization by ethylene oxide persisted in the presence of large amounts of nitric oxide. It is therefore concluded that maximum inhibition of organic decomposition reactions by nitric oxide does not in all cases correspond to complete suppression of chains, and hence the real chain length in such reactions may be greater than that inferred from the results of the nitric oxide inhibition method.

Introduction

Free radicals have been detected in the high temperature thermal decomposition of the hydrocarbons by Paneth, Rice, and their co-workers [see (19)], and it has been suggested by Rice that most organic compounds, and specifically the hydrocarbons, decompose by a free-radical mechanism at lower temperatures. While the evidence in a general way supports Rice's conclusions, the specific mechanisms proposed by Rice and Herzfeld (18) have been shown in a number of cases to be untenable (15–17, 21–23, 30–33). The subject has recently been reviewed in detail (14, 28, 29), and the general aspects of the problem will therefore not be further discussed here.

In view of the importance of the question, and of the uncertainty which surrounds it, other methods of attack are of great importance. One such method which has had considerable success is the use of nitric oxide as a test for the presence of free-radical chains in organic decomposition reactions. It was found by Staveley and Hinshelwood (27) that while large amounts of added nitric oxide catalyzed many organic decomposition reactions, small amounts often caused some inhibition. They assumed that the maximum inhibition corresponds to the complete suppression of chains normally present, and thus calculated mean chain lengths of from two to twenty for a number of decomposition reactions. This is definite evidence for the presence of chains, but in most cases the chain lengths thus obtained are far too small to be in accord with the Rice-Herzfeld mechanisms. The main defect of the nitric oxide inhibition method is that the assumption that maximum

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inhibition corresponds to a complete supression of all chains is arbitrary, and makes the calculated chain lengths of somewhat doubtful significance.

A number of investigations of the paraffin decompositions have been made by this method. Staveley (26) found marked inhibition of the decomposition of ethane at 620° C. The mean chain length (defined as the ratio of the rate in the absence of nitric oxide to the lowest rate in the presence of nitric oxide) varied from 20.6 at 51 mm. ethane pressure to 6.4 at 501.5 mm. He concluded that in all probability only a few molecules decompose primarily into radicals, but that these lead to very long chains, of the order of 10^5 to 10^7 units.

A further investigation of the effect of nitric oxide on the ethane decomposition at 600° C. was made by Hobbs and Hinshelwood (11). They paid particular attention to the effect of the ethane pressure on the inhibition, and concluded that the inhibition was proportional to $1/(C_2H_6)^{0.35}$. From this they conclude that in the normal decomposition the chains are broken by recombination of radicals in the gas phase, largely with ethane molecules as third bodies. In the presence of nitric oxide the chains are assumed to end by the recombination of a radical with a nitric oxide molecule.

In a further paper (12) Hobbs and Hinshelwood compare the effect of nitric oxide on the decompositions of methane, ethane, propane, and hexane. They find that in all cases the chain length decreases with increasing pressure of the hydrocarbon. The chain lengths found vary from 3.3 to 10.1 for propane, from 1.4 to 2.3 for hexane, and from 2.9 to 4.7 for methane. They conclude that the mean chain length depends upon the relative values of three activation energies, namely, that of radical formation, of decomposition by internal rearrangement, and of chain propagation. Approximate indications are that the last tends to decrease with increasing molecular weight of the hydrocarbon.

Recently Echols and Pease (6) have reported that nitric oxide inhibits the decomposition of *n*-butane. In a later note (7) they conclude that the effect is only transient, and that nitric oxide forms an unstable compound with the chain carriers which breaks down again and gives the radicals back to the system, thus neutralizing the inhibition.

It will be apparent from the above discussion that considerable information regarding the participation of free radicals in decomposition reactions is obtainable from experiments on inhibition by nitric oxide. From a quantitative point of view, however, such experiments suffer from two defects. In the first place the assumption that maximum inhibition corresponds to the complete suppression of chains normally present is arbitrary. In the second place the chain lengths calculated are mean chain lengths, and it is left an open question whether all the decomposing molecules follow a chain mechanism, or whether very few of the primary acts involve a split into radicals but the resulting chains are very long.

Another method of investigation which has been largely used is to cause the sensitized free radical decomposition of a hydrocarbon by the addition to it of a compound which is known to give free radicals when it decomposes.

Thus in the case of *n*-butane, Heckert and Mack (36) found that sensitized decomposition occurred in the presence of decomposing ethylene oxide. Ethylene oxide has been shown to produce methyl radicals by Fletcher (8) and by Fletcher and Rollefson (9). Frey (10) also showed that 1% of dimethyl mercury could set up chains 20 molecules long in *n*-butane at 525° C. Echols and Pease (5) found also that chains were set up in *n*-butane by decomposing ethylene oxide at 425° C. By comparing the ratio of unsaturates to the carbon monoxide formed from the ethylene oxide decomposition, they calculated chain lengths as high as 12. Sickman and Rice (25) found that radicals from the decomposition of azomethane also set up a chain decomposition of *n*-butane.

It was decided that it should be possible to clear up certain of the ambiguities in the interpretation of results obtained by the nitric oxide inhibition method. An investigation has therefore been made of the efficiency of nitric oxide in breaking chains induced in *n*-butane by the addition of ethylene oxide at low temperatures where the normal decomposition of *n*-butane is negligibly slow. The advantage of this method is that under these circumstances the entire decomposition of the butane is by radical chain processes. It should thus be possible to determine unequivocally the efficiency of nitric oxide in suppressing chain processes.

Experimental

The static method was used, and the reaction was followed by observing the rate of change of pressure, and by analysis.

The apparatus was similar in principle to that used in previous investigations [see, for example (34)]. The reaction vessel, of Pyrex, had a capacity of about 600 cc., and the walls were coated with potassium chloride from a 2% aqueous solution at the beginning of the investigation. The capillary manometer was wound with nichrome wire and heated electrically to about 100° C. to prevent condensation of the reaction products. The reaction vessel was heated by an electric furnace, and the temperature was measured with a chromel-alumel thermocouple in conjunction with a potentiometer. The temperature was controlled by manual regulation, and could be maintained constant to within $\pm 1°$.

When the reaction had progressed to the desired extent, the products were collected for analysis by sudden expansion into a bulb of one litre capacity through a liquid air trap. This trap kept the pressure low in the expansion bulb, since most of the products condensed, and thus greatly increased the effective volume of the expansion bulb. Since the expansion was rapid and occurred through narrow tubing, there was no danger of fractionation through diffusion. The samples thus obtained were transferred to a Burrell gas analysis apparatus by means of a Toepler pump and a portable mercury gas holder.

n-Butane was obtained in cylinders from the Ohio Chemical and Mfg. Co., and was fractionally distilled before use. Ethylene oxide was obtained from

the Eastman Kodak Co. Nitric oxide was generated by dropping mercury into a 2% solution of sodium nitrite in concentrated sulphuric acid. The resulting gas was passed over phosphorus pentoxide, and through a trap at −80° C., into a storage reservoir.

Between runs the apparatus was always kept evacuated to avoid possible complications in the acetaldehyde decomposition due to traces of oxygen (13).

Experimental Results

(A) Butane–Nitric-oxide Mixtures

A few experiments were first made on the inhibition of the decomposition of *n*-butane by nitric oxide at 525° C. The inhibiting effect was found to be considerable, in agreement with the work of Echols and Pease. Typical data are shown in Table I. The data lead to a "mean chain length" (calculated on the assumption that maximum inhibition corresponds to the complete suppression of chains) of about 16 at a butane pressure of 20 cm.

TABLE I

THE EFFECT OF NITRIC OXIDE ON THE DECOMPOSITION OF BUTANE AT 525° C.

Initial butane pressure, cm.	Initial nitric oxide pressure, cm.	T_{25}, min.	Initial rate, expressed as pressure increase in mm. per min.	Relative rate
21.50	0.00	19	11.4	1.00
17.42	0.58	36	1.3	0.11
19.76	1.74	45	0.7	0.06
18.30	2.10	44	0.7	0.06

The complete data for the above runs are plotted in Fig. 1. It will be noted that the initial rate of the reaction in the presence of nitric oxide is very slow, but that in the later stages of the reaction there is little or no difference between the rates in the presence and in the absence of nitric oxide. This is in agreement with the conclusions of Echols and Pease. Maximum inhibition appears when the partial pressure of nitric oxide is about 20 mm.

The above results are given merely to show the agreement with those of previous workers. Further work is in progress on this phase of the problem, and the results will be reported in full later.

(B) Butane–Ethylene-oxide Mixtures

The effect of ethylene oxide on butane at 450° C. was next investigated. At this temperature the ordinary decomposition of butane is negligibly slow (the time to quarter value being about 160 hr.), and the sensitizing effect of ethylene oxide can be investigated without complications due to the normal

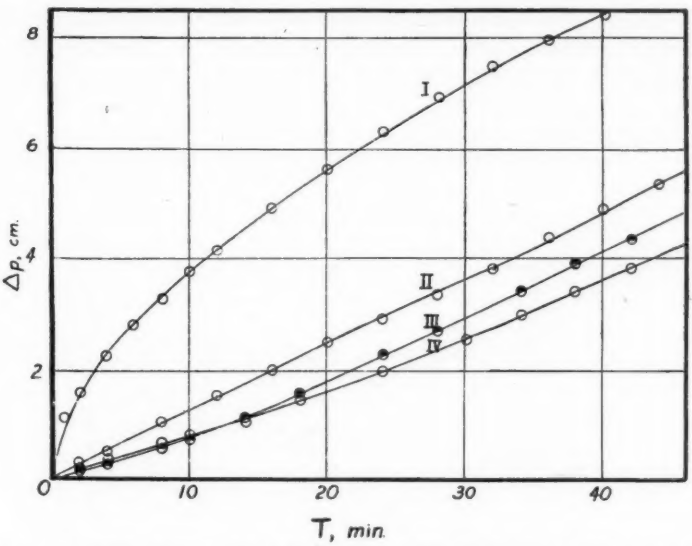

FIG. 1. *Runs at 525° C. whose initial pressures in centimetres are: Curve I. Butane, 21.50. Curve II. Butane, 17.42; NO, 0.58. Curve III. Butane, 19.76; NO, 1.74. Curve IV. Butane, 18.30; NO, 2.10.*

decomposition. Table II gives results for a series of runs made with constant ethylene oxide pressures of about 7 and 3 cm. and mixtures containing varying amounts of butane. The complete data for the experiments with an ethylene oxide pressure of 7 cm. are plotted in Fig. 2.

It will be seen that considerable sensitized decomposition of butane has occurred. A direct calculation from the data in the last column of Table II

TABLE II

THE SENSITIZED DECOMPOSITION OF BUTANE BY ETHYLENE OXIDE AT 450° C.

Initial ethylene oxide pressure, cm.	Initial butane pressure, cm.	$\frac{C_4H_{10}}{(CH_2)_2O}$, approximate ratio	Initial rate of pressure increase, mm. per min.
7.10	0.00	0 : 1	5.04
7.06	7.24	1 : 1	6.63
7.02	13.98	2 : 1	9.66
7.00	27.30	4 : 1	15.0
6.95	52.55	8 : 1	20.4
2.84	0.00	0 : 1	2.5
2.87	2.93	1 : 1	5.4
2.80	5.95	2 : 1	7.8
3.00	12.10	4 : 1	12.3
2.84	43.06	16 : 1	23.0

would indicate that up to 10 molecules of butane are decomposed for each molecule of ethylene oxide. Actually the chain lengths must be greater than this for two reasons. In the first place, according to Fletcher and Rollefson (9) only a fraction of the ethylene oxide molecules give rise to radicals

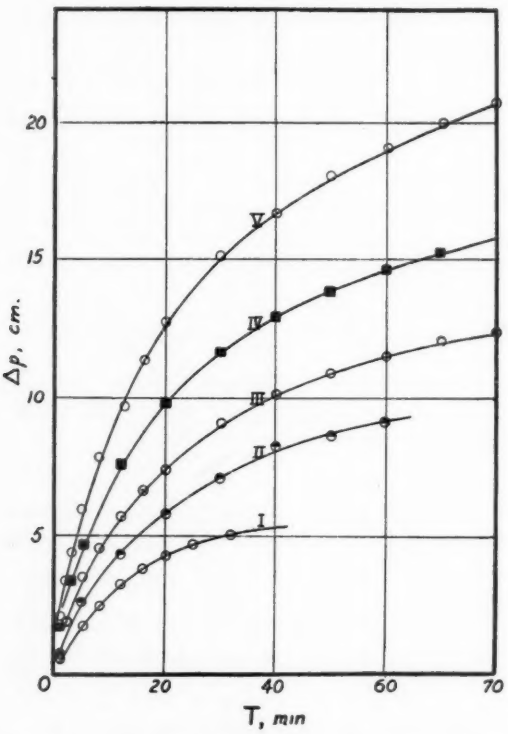

FIG. 2. *Butane–ethylene-oxide runs at 450° C. Ethylene oxide at a constant initial pressure (approx. 7 cm.)*

Curve	*I*	*II*	*III*	*IV*	*V*
Approx. ratio butane/ethylene oxide	*0 : 1*	*1 : 1*	*2 : 1*	*4 : 1*	*8 : 1*

in decomposing. This will make the chain lengths higher than a direct calculation would indicate.

There is also a second reason why the apparent chain length is too small. Heckert and Mack in their original work on the ethylene oxide decomposition noted that in 1 : 2.3 ethylene-oxide–butane mixtures the rate of the ethylene oxide decomposition was only about one-half that of ethylene oxide alone. It is not therefore justifiable to infer the amount of ethylene oxide decomposing in an ethylene-oxide–butane mixture from the rate of its normal decomposition. It follows that an accurate determination of the chain length can be made only by determining by analysis the relative amounts of ethylene oxide and

of butane decomposed. We have, therefore, as have Echols and Pease, determined the relative amounts of carbon monoxide and of unsaturated hydrocarbons in the products, and we will use the ratio C_nH_{2n}/CO as a measure of the relative amounts decomposed. Actually, of course, the initial products are what should be determined, but in order to obtain sufficiently large samples for analysis we have determined the values of the ratio at quarter-time. The analyses were made with cuprous chloride as an absorbent for carbon monoxide, and fuming sulphuric acid for unsaturates. Fuming sulphuric acid also absorbs a little butane, but this can be corrected for by means of blank experiments with pure butane. The results of the analyses are given in Table III.

TABLE III

BUTANE–ETHYLENE-OXIDE MIXTURES AT 450° C.
ANALYSES AT T_{25}

Approximate ratio $\frac{\text{butane}}{(CH_2)_2O}$	Mole per cent		$\frac{\text{Unsaturates}}{CO}$
	Unsaturates	CO	
8	18.2	3.2	5.7
	18.7	3.5	5.4
4	16.4	3.6	4.6
	17.4	3.7	4.6
2	16.5	5.7	2.9
	17.0	7.1	2.4
1	14.1	7.4	1.9
	13.6	7.2	1.9

If we assume that the products at the start of the reaction are the same as those at quarter-time, we can calculate from the data of Table II how much of the pressure increase is to be apportioned to the ethylene oxide decomposition and how much to that of butane. Actually this assumption is open to some objection, but it cannot be very far wrong. We thus get the data of Table IV.

TABLE IV

CHAIN LENGTHS IN ETHYLENE-OXIDE–BUTANE MIXTURES

Approximate ratio $\frac{\text{butane}}{(CH_2)_2O}$	Initial rate, mm. per min.	Ethylene oxide decomposition, mm. per min.	Butane decomposition, mm. per min.	Chain length
0 : 1	5.0	5.0	0.0	—
1 : 1	6.6	2.3	4.3	2.9
2 : 1	9.7	2.7	7.0	4.9
4 : 1	15.0	2.7	12.3	8.3
8 : 1	20.4	3.1	17.3	11.5

It will be seen that the apportionment of the rate of pressure increase on the basis of the analyses leads to the conclusion that the initial rate of decomposition of ethylene oxide in the presence of butane is only about one-half the normal rate. No great significance is to be attached to the drift of the last four figures in Column 3 of Table IV, since the assumption that the initial products are the same as those at quarter-time is only approximate.

In the calculation of the chain length from the data of Columns 3 and 4 of Table IV, consideration must be given to the mechanism of the ethylene oxide decomposition. According to Fletcher and Rollefson (9), in the ordinary decomposition of ethylene oxide 0.3 methyl radicals are formed per molecule of ethylene oxide decomposed. This conclusion is based, in the first place, on Sickman's discussion (24) of the mechanism of the ethylene oxide decomposition. He concluded that the complexities in the reaction could be explained on the assumption that the mechanism is

$$\begin{aligned}
&(1) && (CH_2)_2O = 2R\\
&(2) && (CH_2)_2O = CH_3CHO\\
&(3) && R + CH_3CHO = RH + CH_3CO = RH + CO + R\\
&(4) && 2R + M = X + M,
\end{aligned}$$

where R represents a free radical, and M is any third body. All the experimental facts are readily interpreted on this basis if we assume that k_1 is much less than k_2, *i.e.*, that most ethylene oxide molecules isomerize to acetaldehyde, which then undergoes a radical-sensitized decomposition, and that relatively few ethylene oxide molecules give free radicals by Reaction (1). It should be noted that the sensitized decomposition of the acetaldehyde will not affect the radical concentration, since each radical removed by Reaction (3) is regenerated.

It follows that if ethylene oxide is used as a sensitizer in the butane decomposition, the chain length will not be given by

$$\frac{\text{molecules of butane decomposed}}{\text{molecules of ethylene oxide decomposed}},$$

but by

$$\frac{\text{molecules of butane decomposed}}{(\text{molecules of ethylene oxide decomposed}) \cdot F},$$

where F is the number of free radicals produced per molecule of ethylene oxide decomposed. The Sickman mechanism, by requiring k_1 to be much less than k_2, necessitates that F should be much less than 1, and hence that the chain length shall be greater than a direct calculation from the butane–ethylene-oxide ratio would indicate.

Fletcher and Rollefson investigated the ethylene oxide decomposition with special emphasis on the role of free radicals. Their work led them to postulate a mechanism of the type suggested by Sickman, but of a more detailed nature:

$$\begin{aligned}
&(1) && (CH_2)_2O = HCHO + CH_2\\
&(2) && (CH_2)_2O = CH_3CHO\\
&(3) && CH_2 + (CH_2)_2O = 2CH_3 + CO\\
&(4) && CH_3 + CH_3CHO = CH_5 + CH_4 + CO\\
&(5) && 2CH_3 = C_2H_6.
\end{aligned}$$

This mechanism is in good agreement with their rate measurements, analyses for acetaldehyde and formaldehyde, etc. By assuming that all the hydrogen found in the products comes from the decomposition of formaldehyde formed by Reaction (1), and that all the ethane comes from Reaction (5), they calculate that 14% of the ethylene oxide decomposes by Reaction (1). Whence, since each methylene gives rise to two methyls, they conclude that 0.3 methyls are formed for each ethylene oxide molecule decomposed.

While it cannot be said that this mechanism is established, it is undoubtedly plausible, and all the evidence indicates that by no means all the ethylene oxide decomposes by way of free radicals. It seems very unlikely that Fletcher and Rollefson's estimate of the fraction of ethylene oxide molecules giving rise to radicals is too low, although it may well be too high, since hydrogen and ethane may arise in other ways.

Now, the effect of butane in diminishing the rate of the over-all pressure increase, or the over-all production of carbon monoxide, must obviously be due to the suppression of Reaction (4), since butane can compete with acetaldehyde for methyl radicals produced by Reaction (3). Obviously, however, the presence of butane can have no appreciable influence on the primary steps, Reactions (1) and (2). It follows therefore that in the presence of butane the total number of radicals produced per unit time will remain constant, although the total number of molecules of carbon monoxide produced will diminish, as will the total pressure increase. Hence if the pressure increase due to the ethylene oxide decomposition falls in the presence of butane from 5.0 mm. per min. to, say, 3.1 mm. per min., we may assume that the number of radicals produced per carbon monoxide molecule formed rises from 0.3 to $\frac{0.3 \times 5.0}{3.1} = 0.485$. On this basis we obtain the chain lengths given in Column 5 of Table IV. It may be emphasized that these are minimum chain lengths, and that if fewer free radicals are produced than is indicated by the conclusions of Fletcher and Rollefson, the real chain lengths will be greater than those given.

It was pointed out above that it is very unlikely that *more* free radicals are produced from ethylene oxide than Fletcher and Rollefson suggest. Support for this conclusion is obtained from the work of Frey (10), who investigated the butane decomposition sensitized by methyl radicals from the decomposition of dimethyl mercury. On the assumption that two methyl radicals are formed for each molecule of mercury dimethyl decomposed, he estimated a chain length of about 20. Since there is little doubt that methyl radicals are also the chain carriers in the ethylene oxide sensitized decomposition, it is unlikely that the chain length should be very different from that obtained in Frey's work. Furthermore, the work of Cunningham and Taylor (1) on the decomposition of mercury dimethyl indicates the possibility that only a portion of the mercury dimethyl molecules give radicals. There is thus the possibility that the real chain length in Frey's work was considerably greater than 20. It therefore appears very unlikely that the chain

length in the ethylene oxide sensitized decomposition should be less than 10, and it is quite probable that it is greater than this value.

(C) Ethylene-oxide–Nitric-oxide Mixtures

Before proceeding to a study of the three component mixtures it was obviously necessary to investigate the effect of nitric oxide on the rate of decomposition of ethylene oxide. Otherwise it would not be possible to tell whether a diminution in the rate of the sensitized butane decomposition were to be ascribed to a suppression of chain processes in butane, or to an inhibition of the decomposition of the sensitizer. A series of experiments was therefore made with a constant initial pressure of ethylene oxide (7 cm.), and varying amounts of nitric oxide. The complete data of these experiments are plotted in Fig. 3, and the initial rates are given in Table V.

The inhibiting effect of nitric oxide on the ethylene oxide decomposition is evidently considerable, and due allowance must be made for this in considering the three component mixtures.

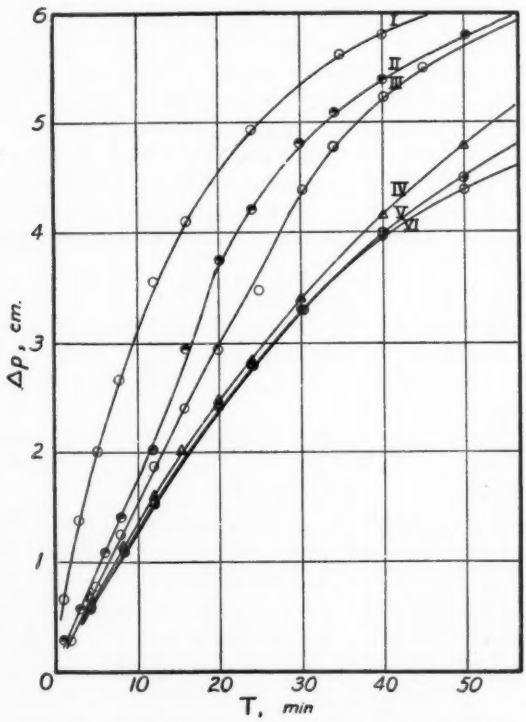

FIG. 3. *Ethylene-oxide–nitric-oxide runs at 450° C. Ethylene oxide at a constant initial pressure (approx. 7 cm.).*

Curve	*I*	*II*	*III*	*IV*	*V*	*VI*
Approx. ratio ethylene oxide/NO	*1 : 0*	*16 : 1*	*8 : 1*	*4 : 1*	*2 : 1*	*1 : 2*

These results are somewhat contrary to the findings of Fletcher and Rollefson who reported that the addition of small quantities of nitric oxide to ethylene oxide increased the induction period but did not change the rate of pressure increase thereafter. In our experiments the induction period was of much smaller duration, and there is no question that the maximum rate of pressure increase was decreased by the addition of nitric oxide. However, our experiments were carried out at a somewhat higher temperature, and the lowest nitric oxide concentration employed by us was about twice the highest concentration employed by them. There seems to be no doubt in any case that, in agreement with the conclusions of Fletcher and Rollefson, the action of nitric oxide is to inhibit the induced decomposition of acetaldehyde, and not the primary process. This is not in accord with the findings of Verhoek (35).

TABLE V

ETHYLENE-OXIDE–NITRIC-OXIDE MIXTURES

Approximate ratio $\frac{\text{ethylene oxide}}{\text{NO}}$	Ethylene oxide pressure, cm.	Nitric oxide pressure, cm.	Initial rate, mm. per min.
1 : 0	7.15	0.00	5.04
16 : 1	7.11	0.41	1.81
8 : 1	7.20	0.95	1.60
4 : 1	7.04	1.80	1.38
2 : 1	7.25	3.65	1.38
1 : 2	6.77	14.67	1.56

Analyses were also made at quarter-time on runs with a 4 : 1 ethylene-oxide–nitric-oxide mixture, and with pure ethylene oxide. These gave values for the ratio

$$\frac{\text{unsaturated hydrocarbons}}{\text{CO}}$$

of 0.012 for pure ethylene oxide, and of 0.015 for the mixture. It is therefore evident that the amount of unsaturates formed from ethylene oxide, both alone and in the presence of nitric oxide, is so small that no appreciable error is introduced when the unsaturates/CO ratio is used as an indication of the relative amounts of butane and of ethylene oxide decomposed. Furthermore, these analyses indicated that at quarter-time a large amount of nitric oxide is still left in the system, in spite of the fact that the inhibition has almost ceased at this stage.

(D) Butane–Ethylene-oxide–Nitric-oxide Mixtures

In these experiments the partial pressure of ethylene oxide was maintained approximately constant at 7 cm. to enable a comparison with the results of the previous section. The butane pressure was maintained constant at 28 cm.,

and the partial pressure of nitric oxide was varied over a wide range. The complete data are plotted in Fig. 4, and the initial rates of pressure increase are given in Table VI.

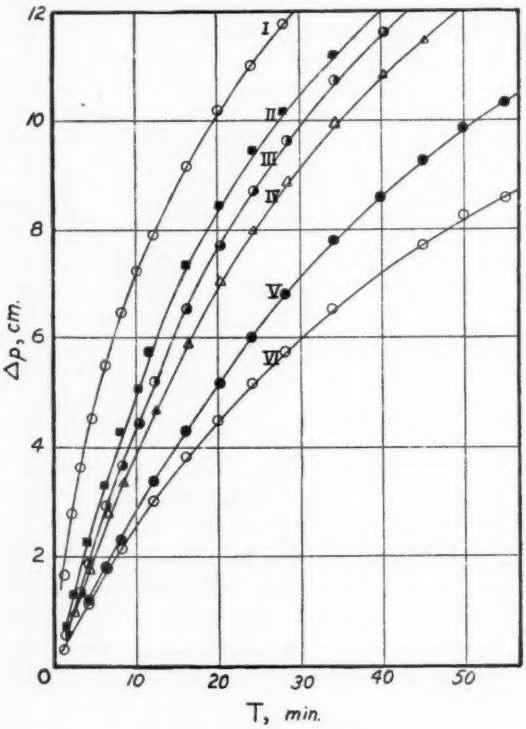

FIG. 4. *Butane–ethylene-oxide–nitric-oxide runs at 450° C. Butane and ethylene oxide at constant initial pressures (approx. 28 cm. and 7 cm. respectively).*

Curve	*I*	*II*	*III*	*IV*	*V*	*VI*
Approx. ratio ethylene oxide/NO	*1 : 0*	*16 : 1*	*8 : 1*	*4 : 1*	*2 : 1*	*1 : 1*

If it is assumed that the ethylene oxide decomposition will proceed at the same rate in the three component mixture as in an ethylene-oxide–nitric-oxide mixture, chain lengths can be calculated from the data of Table VI. The calculations have been made in a manner similar to that used in Section (B), *i.e.*, it is assumed that the inhibiting effect of nitric oxide on the ethylene oxide decomposition results in a lower rate of pressure increase, but does not alter the rate of the primary production of free radicals. We thus arrive at the values given in Column 8. In these calculations we have neglected the inhibiting effect of butane on the ethylene oxide decomposition since this

TABLE VI

BUTANE–ETHYLENE-OXIDE–NITRIC-OXIDE MIXTURES

Butane, cm.	Ethylene oxide, cm.	Nitric oxide, cm.	Approximate ratio $\frac{(CH_2)_2O}{NO}$	Initial rate of pressure increase, mm. per min.	Initial rate in ethylene-oxide-nitric-oxide mixtures	Moles of butane decomposed per mole of ethylene oxide decomposed	Chain length
28.09	6.96	0.00	1 : 0	15.3	(5.04)	—	8.3
27.95	6.96	0.44	16 : 1	6.30	1.81	2.5	3.0
28.30	6.98	0.84	8 : 1	5.17	1.60	2.3	2.5
28.77	7.09	1.78	4 : 1	4.70	1.38	2.4	2.2
28.42	7.18	3.53	2 : 1	3.25	1.38	2.0	1.8
27.86	7.04	7.08	1 : 1	3.04	1.56	1.0	1.0

effect will be small compared to that of nitric oxide. As a result of this approximation the calculated chain lengths may be slightly low. To decide the question analyses were made at quarter-time of the products from the three component mixtures. The results of these are given in Table VII.

All things considered, the agreement of the mean chain lengths with those given in Table VI is quite satisfactory. The values given in Table VII are probably the more reliable. It thus appears that the addition of nitric oxide cuts down the chain length in the ethylene oxide sensitized butane decomposition from about 10 to 1.5, but that no matter how high the nitric oxide concentration may be the chain length cannot be reduced much below this value.

TABLE VII

BUTANE–ETHYLENE-OXIDE–NITRIC-OXIDE MIXTURES. ANALYSES AT T_{25}

Approximate ratio $\frac{(CH_2)_2O}{NO}$	Products, mole per cent			$\frac{C_nH_{2n}}{CO}$	Chain length
	NO	C_nH_{2n}	CO		
1 : 0	—	16.4	3.6	4.6	8.3
	—	17.4	3.7	4.6	8.3
16 : 1	0.31	14.9	5.0	3.0	3.6
	0.52	15.4	6.1	2.5	3.0
4 : 1	1.1	13.2	7.5	1.8	1.65
	0.8	13.9	6.6	2.1	1.9
2 : 1	1.6	12.7	7.9	1.6	1.45
	2.1	12.8	8.9	1.4	1.3
1 : 1	6.4	12.4	8.5	1.5	1.55
	6.3	12.5	8.9	1.4	1.45
1 : 2	14.5	10.4	7.0	1.5	1.55

Discussion

The use of nitric oxide as an indicator for the presence of chains in organic decompositions involves the assumption that maximum inhibition corresponds to the complete suppression of chains. The present results show that this assumption is not entirely justified, since in the ethylene oxide sensitized decomposition of butane maximum inhibition corresponds to a chain length of 1.5 or greater. It is therefore almost certain that maximum inhibition does not correspond to the complete suppression of chains in the normal decomposition of butane, and perhaps also in many other cases. The chain lengths calculated from nitric oxide inhibition must therefore be regarded as minimum chain lengths, and it is possible in any individual case, and particularly so with the hydrocarbons, that the real chain lengths are greater than the nitric oxide method would indicate, and they may be very much greater. On the assumption of Fletcher and Rollefson that 0.3 radicals are formed per ethylene oxide molecule decomposed, the minimum chain length found here is 1.5, which would correspond to 4.0 in the normal decomposition of butane if we assume that two radicals are formed in the primary step. It has been pointed out above, however, that it is quite probable that less radicals are formed in the ethylene oxide decomposition than Fletcher and Rollefson conclude. If this is the case, then the chain length at maximum inhibition in the present investigation is much higher than 1.5, and this may also be true for many other reactions.

As pointed out in the Introduction, there has been considerable discussion as to whether the chain lengths obtained by the nitric oxide inhibition method are to be interpreted as actual chain lengths, or whether they are merely mean values and actually there are very few chains but these are long. It has been suggested in some cases that the real chain lengths are as high as 10^5 to 10^7. It is obvious that in the sensitized decomposition of a substance we have a more or less definite idea of the number of primary acts on the part of the sensitizer, and hence the chain length under these circumstances is the average length of the chains which are really started. Now the chains in the ordinary decomposition of butane are undoubtedly carried by radicals which are the same as, or similar to, those which are effective in the sensitized decomposition. There seems therefore to be no justification for the assumption that the actual chain lengths in the two cases are of quite different orders of magnitude. In our opinion, therefore, there is no justification for the conclusion that there are merely a few very long chains in the normal decomposition of butane. It is perhaps worth pointing out that the assumption of a few very long chains in the ethylene oxide sensitized reaction would lead to difficulties. Thus suppose that we assume a few chains with a length of, say, 10^6 units. Then, since nitric oxide only reduces the mean chain length by a factor of 5 to 10, it would be necessary to assume a chain length of about 10^5 under circumstances corresponding to maximum inhibition by nitric oxide.

It seems to be generally accepted that the mechanism of nitric oxide inhibition is the formation of an addition compound between a radical and nitric

oxide. Various detailed schemes have been proposed in specific cases. The following generalized scheme, proposed by Rice and Polly (20), is in agreement in principle with the suggestions of other workers:

(1) $M_1 = 2\,R_1$
(2) $M_1 + NO = HNO + R_2$
(3) $R_1 + M_1 = R_1H + R_2$
(4) $R_2 = R_1 + M_2$
(5) $R_1 + NO = R_1NO$
(6) $2\,R_1 = R_1R_1$
(7) $R_2 + NO = R_2NO$
(8) $R_1 + R_2 = R_1R_2$

Rice and Polly then suggest two different schemes:

I. Reaction (4) has a low activation energy. The chains therefore end by Reactions (5) and (6).

II. Reaction (4) has a high activation energy, and the chains end by Reactions (7) and (8).

If we accept Scheme II, and assume that Reaction (3) is fast, then chains will be stopped only by combination of R_2 and NO, and not by combination of R_1 and NO. Under these circumstances nitric oxide would be unable to break chains until one link later than the primary step. In the present case, therefore, if it is assumed that maximum inhibition corresponds to a chain length of about 1.5 the result could perhaps be explained on this mechanism, and at maximum inhibition all chains would be suppressed after the second link. However, for the reasons outlined above, it is possible that the chain lengths are much greater than Fletcher and Rollefson's mechanism indicates, and hence that the chain length at maximum inhibition is considerably greater than 1.5. If this is the case it appears that either

(a) Some reaction like (2) is promoting chain decomposition and competing with Reactions (5) or (7) which break chains. Maximum inhibition is therefore a balance between the two opposing factors and does not correspond to the complete suppression of chain processes.

Or

(b) There are two distinct types of chain process, only one of which is susceptible to inhibition by nitric oxide.

In any case the present results cast some suspicion upon the idea that maximum inhibition by nitric oxide in all cases corresponds to complete suppression of chains. The possibility must therefore not be overlooked that free radical chain processes may exist which are not indicated by the action of nitric oxide.

One further point merits discussion. We have found, as did Echols and Pease, that the initial inhibition by nitric oxide falls off with time. Now the decrease in the first order constants in the butane and other hydrocarbon decompositions as a run progresses suggests, as Dintzes and Frost have pointed out (2, 3, 4), that the products of the reaction have an inhibiting effect. Rice

and Polly have recently investigated the inhibiting effect of propylene on a number of reactions and have found that it is quite efficient in suppressing free radical chain processes. It therefore seems likely that as the butane decomposition progresses and the concentration of olefines increases, the inhibiting effect of the olefines will swamp out that of the added nitric oxide, and as a result the rate of the nitric oxide inhibited reaction will approach the normal rate in the later stages of the reaction.

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